# ELEMENTS

OF

# CHEMISTRY,

INCLUDING THE

RECENT DISCOVERIES AND DOCTRINES OF THE SCIENCE.

BY


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*Third American, from the Second London Edition.*

WITH NOTES AND EMENDATIONS,


BY FRANKLIN BACHE, M.D.

Professor of Chemistry in the Franklin Institute of the State of Pennsylvania; one of the Secretaries of the American Philosophical Society, &c.



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D. CALDWELL,
*Clerk of the Eastern District of Pennsylvania.*



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TO

FREDERICK STROMEYER, M.D. F.R.S.E.

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY

OF GOTTINGEN, &c. &c. &c.

My Dear Sir,

Under your guidance I made my first essay in analytical chemistry; from your example I imbibed a taste for chemical research; and to you I am indebted for that practical knowledge of the subject, without which this volume would never have been written. To you, therefore, who have thus so essentially contributed to the undertaking, permit me to inscribe a work, intended to advance the progress of that science which you cultivate with so much zeal and success. Believe me, my dear Sir, this opportunity of publicly expressing my gratitude for your kindness, and my admiration of your distinguished analytical attainments, is a source of much pride and pleasure to your friend and former pupil,

EDWARD TURNER.

38, Upper Gower Street,
*October* 1. 1828.

## ADVERTISEMENT

OF

# THE AMERICAN EDITOR.



IN preparing for the press the present edition of the deservedly popular Elements of Dr Turner, the editor has taken pains to insure its correctness, by a careful revision of the English copy, and attention to the proof-sheets. In the course of his labours, a considerable number of inaccuracies have been detected, the correction of which, in the present edition, will render it more valuable to the student.

The notes of the editor are distinguished by the letter B. They were written as the printing of the work progressed, and under circumstances that precluded the exercise of much research. For the most part they will be found explanatory or supplementary, though occasionally critical. It has, however, been rarely found necessary to differ from the author, who has certainly evinced, in the composition of his treatise, the talents of an accurate chemist, and a neat and perspicuous writer. The annotations might easily have been extended, had it been deemed expedient; but the editor felt unwilling to swell the work by numerous notes, lest any considerable addition to its size might render it less convenient as a manual for the student.

*Philadelphia, May* 1830.

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# INTRODUCTION.

MATERIAL substances are endowed with two nds of properties, physical and chemical; and the study of the phenomena occasioned by them has given rise to two corresponding branches of knowledge, *Natural Philosophy* and *Chemistry*.

The physical properties are either general or secondary. The first are so called because they are common to all bodies; the latter from being observable in some substances only. Among the first may be enumerated extension, impenetrability, mobility, extreme divisibility, gravitation, porosity, and indestructibility.

*Extension* is the property of occupying a certain portion of space. A substance is said to be *extended* when it possesses length, breadth, and thickness. By *impenetrability* is meant that no two portions of matter can occupy the same space at the same moment. Every thing that possesses extension and impenetrability is matter.

Matter, though susceptible of motion, has no power either to move itself, or arrest its progress when an impulse is once communicated to it. This indifference to rest or motion has been expressed by the term *vis inertiæ*, as if it depended on some specific force resident in matter; but it may with greater propriety be regarded as a negative character, in consequence of which matter is wholly given up to the operation of the various forces which are constantly acting upon it.

Matter is divisible to an extreme degree of minuteness. A grain of gold may be beaten out into so fine a leaf as to cover 50 square inches of surface, and contain two millions of visible points; and yet the gold which covers the silver wire used in making gold lace, is spread over a surface twelve times as great. (Nicholson's Introduction to Natural Philosophy, vol. i.) By chemical means a still more minute division may be effected.

A keen controversy existed at one time concerning the divisibility of matter; some philosophers contending that it is infinitely divisible, while others maintained an opposite opinion. Owing to the imperfection of our senses the question cannot be determined by direct experiment, because matter certainly continues to be divisible long after having ceased to be an object of sense. The decision, if effected at all, can only be accomplished by indirect means. In favour of the first view it was urged, that to whatever degree matter is divided, it may still be conceived, in possessing extension, to be divisible into two parts; and the minuteness to which matter may actually be reduced, gave additional weight to this argument. Plausible, however, as this mode of reasoning may appear, the opposite opinion is daily becoming more general. It is now commonly believed that matter consists of

ultimate particles or molecules, which are thought to be indivisible; and according to this belief have received the appellation of *atoms*. (From the privative α and τέμνω I cut.) The grounds of this opinion are derived from certain astronomical phenomena, from the laws of chemical union, and the relations which have been observed to exist between the composition and form of crystallized bodies. These subjects will be considered in their proper place; but I may observe here, in order to show the nature of the argument, that the supposed existence of atoms affords a ready explanation of various well ascertained facts, which otherwise would be totally inexplicable.

All bodies descend in straight lines towards the centre of the earth, when left at liberty at a distance from its surface. The power which produces this effect is termed *gravity*, the *attraction* of *gravitation*, or *terrestrial attraction*; and the force required to separate a body from the surface of the earth, or prevent it from descending towards it, is called its *weight*. Every particle of matter is equally affected by gravity; and therefore the weight of any body will be proportional to the number of ponderable particles which it contains.

The minute particles of which bodies consist are disposed in such a manner as to leave certain intervals or spaces between them, and this arrangement is called *porosity*. These interstices may sometimes be seen by the naked eye, and frequently by the aid of glasses. But were they wholly invisible, it would still be certain that they exist. All substances, even the most compact, may be diminished in bulk either by mechanical force or a reduction of temperature. It hence follows that their particles must touch each other at a very few points only, if at all; for if their contact was so perfect as to leave no interstitial spaces, then would it be impossible to diminish the dimensions of a body, because matter is incompressible and cannot yield.—When therefore a body expands, the distance between its particles is increased; and, conversely, when it contracts or diminishes in size, its particles approach each other.

By *indestructibility* is meant that, according to the present laws of nature, matter never ceases to exist. This statement seems at first view contrary to fact. Water and volatile substances are dissipated by heat, and lost; coals and wood are consumed in the fire, and disappear. But in these and all similar phenomena not a particle of matter is annihilated. The apparent destruction is merely owing to a change of form or composition; for the same material particles, after having undergone any number of such changes, may still be proved to possess the characteristic properties of matter.

The secondary properties of matter are opacity, transparency, softness, hardness, elasticity, colour, density, solidity, fluidity, and the like. The condition of bodies with respect to several of these properties seems dependent on the operation of two opposite forces —cohesion and repulsion. To understand how the particles of a body can attach themselves to one another and form a whole, we must suppose them endowed with a power of reciprocal attraction. This force is called *cohesion*, *cohesive attraction*, or the *attraction of aggregation*, in order to distinguish it from terrestrial attraction. Gravity is exerted between different masses of matter, and acts at sensible and frequently at very great distances; while cohesion exerts its influence only at insensible and infinitely small distances. It enables similar molecules to cohere, and tends to keep them in that condition. It is best exemplified by the resistance which a hard body, such as iron or marble, affords to being broken by any external force.

The tendency of cohesion is manifestly to bring the ultimate particles of bodies into immediate contact: and such would be the result of its influence, were it not counteracted by an opposing force, a principle of repulsion, which prevents their approximation. It is a general opinion among philosophers, supported by very strong facts, that this repulsion is owing to the agency of caloric, which is somehow attached to the elementary molecules of matter, causing them to repel one another. Material substances are therefore subject to the action of two contrary and antagonizing forces, one tending to separate their particles, the other to bring them into closer proximity*. The form of bodies, as to solidity and fluidity, is determined by the relative intensity of these powers. Cohesion predominates in solids, in consequence of which their particles are prevented from moving freely on one another. The particles of a fluid, on the contrary, are far less influenced by cohesion, being free to move on each other with very slight friction. Fluids are of two kinds, elastic fluids or aeriform substances, and inelastic fluids or liquids. Cohesion seems wholly wanting in the former; they yield readily to compression, and expand when the pressure is removed; indeed, the space they occupy is chiefly determined by the force which compresses them. The latter, on the contrary, do not yield perceptibly to ordinary degrees of compression, nor does an appreciable dilatation ensue from the removal of pressure, the tendency of repulsion being in them counterbalanced by cohesion.

Matter is subject to another kind of attraction different from those yet mentioned, termed *Chemical attraction* or *affinity*. Like cohesion it acts only at insensible distances, and thus differs entirely from gravity. It is distinguished from cohesion by being exerted between dissimilar particles only, while the attraction of cohesion unites similar particles. Thus, a piece of marble is an aggregate of smaller portions of marble attached to one another by cohesion, and the parts so attached are called *integrant* particles; each of which, however minute, is as perfect marble as the mass itself. But the integrant particles consist of two substances, lime and carbonic acid, which are different from one another as well as from marble, and are united by chemical attraction. They are the *component* or *constituent* parts of marble. The integrant particles of a body are therefore aggregated together by cohesion; the component parts are united by affinity.

The chemical properties of bodies are owing to affinity, and every chemical phenomenon is produced by the operation of this principle. Though it extends its influence over all substances, yet it affects them in very different degrees, and is subject to peculiar modifications. Of three bodies, A, B, and C, it is often found that B and C evince no affinity for one another, and therefore do not combine; that A, on the contrary, has an affinity for B and C, and can enter into separate combination with each of them; but that A has a greater attraction for C than for B, so that if we bring C in contact with a compound of A and

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* It should be borne in mind, however, that the force which tends to bring the elementary molecules into closer proximity, is derived from an innate property of ponderable matter; while the force which tends to separate them is dependent on the operation of a distinct principle, caloric, whose particles, being self-repellent, force the ponderable particles apart. In order to explain why the caloric remains attached to the ponderable molecules, it is necessary to suppose that its particles, though self-repellent, have an attraction for ponderable matter. B.

B, A will quit B and unite by preference with C. The union of two substances is called *combination;* and its result is the formation of a new body endowed with properties peculiar to itself, and different from those of its constituents. The change is frequently attended by the destruction of a previously existing compound, and in that case *decomposition* is said to be effected.

The operation of chemical attraction, as thus explained, obviously lays open a wide and interesting field of inquiry. One may study, for example, the affinity existing between different substances; an attempt may be made to discover the proportion in which they unite; and finally, after collecting and arranging an extensive series of insulated facts, general conclusions may be deduced from them. Hence chemistry may be defined the science, the object of which is to examine the relations that affinity establishes between bodies, ascertain with precision the nature and constitution of the compounds it produces, and determine the laws by which its action is regulated.

Material substances are divided by the chemist into simple and compound. He regards those bodies as compound which may be resolved into two or more parts, and those as simple or elementary, which contain but one kind of ponderable matter. The number of the latter amounts only to fifty-two; and of these all the bodies in the earth, as far as our knowledge extends, are composed. The list, a few years ago, was somewhat different from what it is at present; for the acquisition of improved methods of analysis has enabled chemists to demonstrate that some substances, which were once supposed to be simple, are in reality compound; and it is probable that a similar fate awaits some of those which are at present regarded as simple.

The composition of a body may be determined in two ways, analytically or synthetically. By the first method, the elements of a compound are separated from one another, as when water is resolved by the agency of galvanism into oxygen and hydrogen; by the second, they are made to combine, as when oxygen and hydrogen unite by the electric spark, and generate a portion of water. Each of these kinds of proof is satisfactory; but when they are conjoined,—when we first resolve a particle of water into its elements, and then reproduce it by causing them to unite, the evidence is in the highest degree conclusive.

I have followed, in the composition of this Treatise, the same general arrangement which I adopt in my lectures. It is divided into four principal parts. In the first I shall treat of the *Imponderables*,—agents of so diffusible and subtile a nature, that the common attributes of matter cannot be perceived in them. They are altogether destitute of weight; at least, if they possess any, it cannot be discovered by our most delicate balances. They cannot be confined and exhibited in mass like ordinary bodies; they can be collected only through the intervention of other substances. Their title to be considered material is therefore questionable, and the effects produced by them have accordingly been attributed by some to certain motions or affections of common matter. It must be admitted, however, that they appear to be subject to the same powers that act on matter in general, and that some of the laws which have been determined concerning them, are exactly such as might have been anticipated on the supposition of their materiality. It hence follows, that we need only regard them as subtile species of matter, in order that the phenomena to which they give rise may be explained in the language, and according to the principles which are applied to material substances in general; and I shall therefore consider them such in my subsequent remarks.

The second part comprises *Inorganic Chemistry.* It includes the doctrine of affinity, and the laws of combination, together with the chemical history of all the elementary principles hitherto discovered, and of those compound bodies which are not the product of organization. The elementary bodies are divided into the non-metallic and metallic; and the substances contained in each division are treated in the order which, it is conceived, will be most convenient for the purposes of teaching. From the important part which oxygen plays in the economy of nature, it is necessary to begin with the description of that principle; and from the tendency it has to unite with other bodies, as well as the importance of the compounds it forms with them, it will be useful, in studying the history of each elementary body, to describe the combinations into which it enters with oxygen gas. The remaining compounds which the non-metallic substances form with one another, will next be considered. The description of the individual metals will be accompanied by a history of their combinations, first with the simple non-metallic bodies, and afterwards with one another. The last division of this part will comprise a history of the salts.

The third general division of the work is on *Organic Chemistry*, a subject which will be conveniently discussed under two heads, the one comprehending the products of vegetable, the other of animal life.

The fourth part contains brief directions for the performance of analysis.

# ELEMENTS

OF

# CHEMISTRY.

## PART I.

### SECTION I.

#### *CALORIC.*

THE term *Heat*, in common language, has two meanings: in the one case, it implies the sensation experienced on touching a hot body; in the other, it expresses the cause of that sensation. To avoid any ambiguity that may arise from the use of the same expression in two such different senses, it has been proposed to employ the word *Caloric* to signify exclusively the principle or cause of the feeling of heat, and the use of this term has now become so general, that I have adopted it in the present treatise.

Caloric, on the supposition of its being material, is a subtile fluid, the particles of which repel one another, and are attracted by all other substances. It is imponderable; that is, it is so exceedingly light that a body undergoes no appreciable change of weight, either by the addition or abstraction of caloric. It is present in all bodies, and cannot be wholly separated from them. For if we take any substance whatever, at any temperature, however low, and transfer it into an atmosphere, whose temperature is still lower, a thermometer will indicate that caloric is escaping from it. That its particles repel one another, is proved by observing that it flies off from a heated body; and that it is attracted by other substances, is equally manifest from the tendency it has to penetrate their particles, and be retained by them.

Caloric may be transferred from one body to another. Thus, if a cup of mercury at 60° be plunged into hot water, caloric passes rapidly from one into the other, until the temperature in both is the same; that is, till a thermometer placed in each stands at the same height. All bodies on the earth are constantly tending to attain an equality, or what is technically called an *equilibrium* of temperature. If, for example, a number of substances of different temperatures be enclosed in an apartment, in which there is no actual source of caloric, they will very soon acquire an equilibrium, so that a thermometer will stand at the same point in all of them. The varying sensations of heat and cold, which we experience, are owing to a like cause. On touching

a hot body, caloric passes from it into the hand, and excites the feeling of warmth; when we touch a cold body, caloric is communicated to it from the hand, and thus produces the sensation of cold.

As the transportation of caloric is constantly going forward, it is important to determine by what means, and according to what laws, the equilibrium is established. When any substance is brought into contact with another, which differs from it in temperature,—if, for example, a cold bar of iron be thrust among glowing embers, or a hot ball of the same metal be plunged into a basin of cold water,—the excess of caloric in the hot body passes rapidly to the particles on the surface of the other; from them it is transferred to those situated more internally, and so forth, till the bar in the one case, and the ball in the other arrive at the same temperature as the embers or the water with which they are in contact. In such instances, caloric is said to pass by *communication*, or to be *communicated* from one body to another; and in its passage through any one of those bodies, it is said to be *conducted* by them.

But when a heated substance is placed under such circumstances as to preclude the possibility of its caloric being communicated,—for instance, when a glass globe full of hot water is suspended in the vacuum of an air-pump,—the excess of its caloric still passes away, and in a very short time it will have acquired the temperature of the surrounding objects. It must then be capable of passing from one body to another situated at a sensible distance; it is projected as it were from one to the other. In order that its passage should take place in this manner, it is not necessary that the body should be in vacuo; it passes with equal facility through the air as through a vacuum.

It follows, therefore, that in establishing an equilibrium of temperature, caloric is distributed among the surrounding objects in two ways; partly through the means of intermediate bodies, or by *communication*, partly in consequence of an interchange established from a distance, or by *radiation*.

## *Communication of Caloric.*

Caloric passes through bodies with different degrees of velocity. Some substances oppose very little impediment to its passage, while it is transmitted slowly by others. Daily experience teaches, that though we cannot leave one end of a rod of iron for some time in the fire, and then touch its free extremity, without danger of being burnt; yet this may be done with perfect safety with a rod of glass or of wood. The caloric will speedily traverse the iron bar, so that at the distance of a foot from the fire, it is impossible to support its heat; while we may hold a piece of red hot glass two or three inches from its extremity, or keep a piece of burning charcoal in the hand, though the part in combustion is only a few lines removed from the skin. The observation of these and similar facts, has led to a division of bodies into *conductors* and *non-conductors* of caloric. The former division, of course, includes those bodies which allow caloric to pass freely through their substance, such as metals; and the latter comprises those which do not give an easy passage to it, such as stones, glass, wood and charcoal.

Various methods have been adopted for determining the relative conducting power of different substances. The mode adopted by Ingenhouz,* who made experiments on this subject, is the following.

* Ingenhouz, Journal de Phys. 1789, p. 68.

He covered small rods of the same form, size, and length, but of different materials, with a layer of wax, plunged their extremities into heated oil, and noted to what distance the wax was melted on each during the same interval. The metals were found, by this method, to conduct caloric better than any other substances; and of the metals, silver is the best conductor; gold comes next, then tin and copper, which are nearly equal; then iron, platinum and lead.

Some experiments have lately been made by M. Despretz, apparently with great care, on the relative conducting power of the metals and some other substances, and the results are contained in the following table. (An. de Ch. et Ph. xxxvi. 422.)

| | | | | | |
|---|---|---|---|---|---|
| Gold | . | 1000 | Tin | . | 303.9 |
| Silver | . | 973 | Lead | . | 179.6 |
| Copper | . | 898.2 | Marble | . | 23.6 |
| Platinum | . | 381* | Porcelain | . | 12.2 |
| Iron | . | 374.3 | Fine clay | . | 11.4 |
| Zinc | . | 363 | | | |

The substances employed for these experiments were made into prisms of the same form and size. To one extremity a regular source of heat was applied, and the passage of caloric along the bar was estimated by small thermometers placed at regular distances, with their bulbs fixed in the substance of the prism.

An ingenious plan was adopted by Count Rumford† for ascertaining the relative conducting powers of the different materials employed for clothing. He enveloped a thermometer in a glass cylinder blown into a ball at its extremity, and filled the interstices with the substance to be examined. Having heated the apparatus to the same temperature in every instance by immersing it in boiling water, he transferred it into melting ice, and observed carefully the number of seconds which elapsed during the passage of the thermometer through 135 degrees. When there was air between the thermometer and cylinder, the cooling took place in 576 seconds; when the interstice was filled with fine lint, it took place in 1032″; with cotton wool in 1046″; with sheep's wool in 1118″; with raw silk in 1284″; with beaver's fur in 1296″; with eider down in 1305″; and with hare's fur in 1315″. The general practice of mankind is therefore fully justified by experiment. In winter we retain the animal heat as much as possible by covering the body with bad conductors, such as silk or woollen stuffs; and in summer, cotton or linen articles are employed with an opposite intention.

A variety of familiar phenomena arise from the difference of conducting power. Thus if a piece of iron and glass be heated to the same degree, the sensation they communicate to the hand is very different; the iron will give the sensation of burning, while the glass feels but moderately warm. The quantity of caloric, which in a given time may be brought to the surface of the heated body, so as to pass into the skin, is much greater in the iron than in the glass, and there-

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* In the table as it originally stood in the second English edition of this work, the conductibility of platinum is made superior even to that of silver. Dr Turner very justly remarks, "There must certainly be some mistake in the experiments or calculations of M. Despretz, or in the report of them;" and in this Dr Turner is perfectly correct. Upon consulting Berzelius's Traité de Chimie, M. Despretz's table is given, and the number for platinum stated at 381. I have restored to platinum its proper place and number in the table, and cancelled so much of the author's text as relates to the error. B.

† Rumford, Phil. Tr. 1792.

fore in the former case the sensation must be more acute. This proves that the sense of touch is a very fallacious test of heat and cold; and hence, on applying the hand to various contiguous objects, we are very apt to form wrong notions of their temperature. The carpet will feel nearly as warm as the hand; a book will feel cool, the table cold, the marble chimney-piece colder, and the candle-stick colder still; yet, a thermometer applied to them will stand in all at exactly the same elevation. They are all colder than the hand; but those that carry away caloric most rapidly, excite the strongest sensation of cold.

The conducting power of solid bodies does not seem to be related to any of the other properties of matter; but it approaches nearer to the ratio of their densities than to that of any other property. Count Rumford found a considerable difference in the conducting power even of the same material, according to the state in which it was employed. His observations seem to warrant the conclusion, that in the same substance the conducting power increases with the compactness of structure.

Liquids may be said, in one sense of the word, to have the power of communicating caloric with great rapidity, and yet they are very imperfect conductors. The transmission of caloric from particle to particle does in reality take place very slowly; but in consequence of the mobility of their particles upon each other, there are peculiar internal movements, which under certain circumstances may be occasioned in them by increase of temperature, and which do more than compensate for the imperfect conducting power with which they are really endowed.

When certain particles of a liquid are heated they expand, and thus become specifically lighter than those which have not yet received an increase of temperature; and consequently, according to a well-known law in physics, the colder and denser particles descend, while the warmer ones are pressed upwards. It therefore follows that if caloric enter at the bottom of a vessel containing any liquid, a double set of currents must be immediately established, the one of hot particles rising towards the surface, and the other of colder particles descending to the bottom. Now these currents take place with such rapidity, that if a thermometer be placed at the bottom, and another at the top of a long jar, the fire being applied below, the upper one will begin to rise almost as soon as the lower. Hence, under certain circumstances, caloric is rapidly communicated through liquids.

But if, instead of heating the bottom of the jar, the caloric is made to enter by the upper surface, very different phenomena will be observed. The intestine movements cannot now be formed, because the heated particles have a tendency to remain constantly at the top; the caloric can descend through the fluid only by transmission from particle to particle, a process which takes place so very tardily, as to have induced Count Rumford to deny that water can conduct at all. In this he was mistaken; for the opposite opinion has been successfully supported by Dr Hope, Dr Thomson, and the late Dr Murray, though they all admit that water, and liquids in general, mercury excepted, possess the power of conducting caloric in a very slight degree.

It is extremely difficult to estimate the conducting power of aeriform fluids. Their particles move so freely on each other, that the moment a particle is dilated by a caloric, it is pressed upwards with great velocity by the descent of colder and heavier particles, so that an ascending and descending current is instantly established. Besides, these bodies allow a passage through them by radiation. Now the quantity of caloric which passes by these two channels is so much

greater than that which is conducted from particle to particle, that we possess no means of determining their proportion. It is certain, however, that the conducting power of gaseous fluids is exceedingly imperfect, probably even more so than that of liquids.

## *Radiation.*

When the hand is placed beneath a hot body suspended in the air, a distinct sensation of warmth is perceived, though from a considerable distance. This effect does not arise from the caloric being conveyed by means of a hot current; for all the heated particles have a uniform tendency to rise. Neither can it depend upon the conducting power of the air; since aerial substances possess that power in a very low degree, while the sensation in the present case is excited almost on the instant. There is yet another mode by which caloric passes from one body to another; and as it takes place in all gases, and even in vacuo, it is inferred that the presence of a medium is not necessary to its passage. This mode of transmission is called *Radiation* of Caloric, and the fluid so transmitted is called *Radiant*, or *Radiated Caloric*. It appears, therefore, that a heated body suspended in the air cools, or is brought down to an equilibrium with surrounding bodies, in three ways; first, by the conducting power of the air, whose influence is very trifling; secondly, by the mobility of the air in contact with it; and thirdly, by radiation.

Caloric is emitted from the surface of a hot body equally in all directions, and in right lines, like radii drawn from the centre to the circumference of a circle; so that a thermometer placed at the same distance on any side would stand at the same point, if the effect of the ascending current of hot air could be averted. The calorific rays, thus distributed, pass freely through a vacuum and the air, without being arrested by the latter or in any way affecting its temperature. When they fall upon the surface of a solid or liquid substance, they are either reflected from it, and thus receive a new direction, or they lose their radiant form altogether, and are absorbed. In the latter case, the temperature of the receiving substance is increased, in the former it is unchanged.

The absorption of radiant caloric may be proved by placing a thermometer before the fire, or any heated body, when the mercury will be seen to rise in the stem. It has been ascertained by accurate experiment, and may be demonstrated mathematically, that the intensity of effect diminishes according to the squares of the distance from the radiating point. Thus the thermometer will indicate four times less heat at two inches, nine times less at three inches, and sixteen times less at four inches, than it did when it was only one inch from the heated substance.

The existence of a reflecting power may be shown in a familiar manner, by standing at the side of a fire in such a position that the caloric cannot reach the face directly, and then placing a large plate of tinned iron opposite the grate, and at such an inclination as permits the observer to see in it the reflection of the fire; as soon as it is brought to this inclination, a distinct impression of heat will be perceived upon the face. If a line be drawn from the heated substance to the point of a plane surface from which it is reflected, and a second line from that point to the spot where it produces its effect, the angles which these lines form with a line perpendicular to the reflecting plane are equal to each other, or, in philosophical language, the angle of incidence is equal to the angle of reflection. It is on account

of this law that when a heated body is placed in the focus of a concave parabolic reflector, the diverging rays which strike upon it assume a parallel direction with respect to each other; and when these parallel rays impinge upon a second concave reflector, standing opposite to the former, they are made to converge, so as to meet in its focus, where a great degree of heat is developed. This fact, as applied to the sun's rays or red hot bodies, has been long known. But it is a modern discovery that caloric emanates in invisible rays, which are subject to the same laws of reflection as those that are accompanied by light.

This fact may be inferred from the experiments of the Florentine Academicians, and Lambert observed the reflection of non-luminous caloric; but the honour of establishing it in a decisive and unequivocal manner is due to Messrs. Saussure and Pictet* of Geneva, the latter of whom, at the suggestion of the former, first proved it of an iron ball heated so as not to be luminous even in the dark, and afterwards of a vessel of boiling water. For a knowledge of the laws of radiation in general, however, we are indebted to the researches of Professor Leslie, described in his Essay on Heat.

Mr Leslie employed a hollow tin cube filled with hot water as the radiating substance. The rays proceeding from it were brought, by means of a concave mirror, into a focus, in which the bulb of a differential thermometer was placed. He found that certain substances radiate caloric much more rapidly than others, and that the nature of the surface of a heated body has a singular influence upon its radiation. By adapting thin plates of different metals to the sides of the tin cube, and turning them successively towards the mirror, he found a very variable effect produced upon the thermometer. A bright smooth polished metallic surface radiated caloric very imperfectly; but if the surface was in the least degree dull or rough, the radiating power was immediately augmented. By covering the tin surface with a thin layer of isinglass, paper, wax, or resin, its power of radiation increased surprisingly. Metallic substances were observed to be the worst possible radiators, particularly such as are susceptible of a high polish, as gold, silver, tin, and brass; but it is easy to make them radiate well by giving them the opposite properties, either by scratching their surface, or covering it with whiting, lamp-black, or any other convenient substance. It is commonly supposed that black surfaces radiate better than white ones, but I am not acquainted with any conclusive experiments in proof of this opinion.

Mr Leslie next examined the power of different substances in reflecting caloric, and he soon arrived at the interesting conclusion, that those surfaces which radiate least reflect most powerfully. A polished plate of tin or brass is an excellent reflecting surface, but a bad radiating one; by removing the polish in any way, its reflecting power is diminished in the same proportion as its radiating power is increased. His experiments, indeed, justify the conclusion, that the faculty of radiation is inversely as that of reflection.

There are only two modes by which calorific rays, falling upon a solid opake body, can dispose of themselves; they must either be reflected from it, or enter into its substance. In this case caloric is said to be absorbed. Now it is manifest, that those rays which are reflected cannot be absorbed; and those which are not reflected, must be absorbed. Hence it follows that the absorption of caloric in the same body is inversely as its reflection; and since the property of ra-

* Pictet's Essai sur le Feu, p. 65, (1790.)

diation is likewise inversely as that of reflection, the power of radiating and absorbing caloric must be proportional and equal*.

In speaking of radiant caloric, it is necessary to distinguish calorific rays accompanied by light from those which are emitted by a non-luminous body, since their properties are not exactly similar. Thus the absorption of luminous caloric, whether proceeding from the sun or a common fire, is very much influenced by colour; it is most considerable in black and dark coloured surfaces, while it is much less in white ones. The influence of colour, on the contrary, over the absorption of non-luminous caloric is exceedingly slight; it remains to be proved, indeed, whether any effect can fairly be attributed to this cause.

It may be asked, since radiant caloric passes without interruption through the air, whether it can pass in a similar manner through solid transparent media, such as glass or rock-crystal. The only point of view under which this subject can be considered at present, is with respect to radiant caloric emitted by a warm body that is not luminous. When a piece of clear glass is placed between such a body and a thermometer, the latter is not nearly so much affected as it would be were no screen interposed; and the glass itself becomes warm. These facts prove that at least the greater part of the calorific rays is intercepted by the glass. But the thermometer is affected to a certain degree; and the question is, by what means do the rays reach it? Professor Leslie contends, that all the rays which fall upon the glass are absorbed by it, pass through its substance by its conducting power, and are then radiated from the other side of the glass towards the thermometer, an opinion which Dr Brewster has ably supported by an argument suggested by his optical researches. (Phil. Trans. for 1816, p. 106.) The experiments of Delaroche, on the contrary, (Biot. Traité de Physique, v. 4.) lead to the conclusion that glass does transmit some calorific rays, the number of which, in relation to the quantity absorbed, is greater as the intensity of the heat increases; and the general result obtained by that philosopher agrees with some experiments which Dr Christison and myself performed in the year 1824 on the same subject.

The facts that have been determined concerning the laws of radiant caloric have given rise to two ingenious modes of accounting for the tendency of bodies to acquire an equilibrium of temperature. This takes place, according to M. Pictet, in consequence of the hot body giving calorific rays to the surrounding colder ones till an equilibrium is established, at which moment the radiation ceases. M. Prevost,† on the contrary, contends that radiation goes on at all times, and from all bodies, whether their temperature is the same or different from those that surround them. According to this view, the temperature of a body falls whenever it radiates more caloric than it

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* The remarks of the author on the passage of caloric through surfaces, may, perhaps, be extended with advantage. Surfaces, as to the transmission of caloric, may be divided into two sets; 1st, those which offer an easy passage to caloric, either inwards or outwards; and 2d, those through which caloric passes with difficulty. The first set of surfaces are at the same time good absorbers and radiators; the second set combine the qualities of good reflectors and retainers. The absorbing and radiating power on the one hand, and the reflecting and retaining power on the other, would therefore seem to be common properties, belonging to two distinct sets of surfaces. B.

† Recherches sur la Chaleur.

absorbs; its temperature is stationary when the quantities emitted and received are equal; and it becomes warm when the absorption exceeds the radiation. A hot body, surrounded by others colder than itself, is an example of the first case; the second happens when all the substances which are near one another have the same temperature; and the third occurs when a cold body is brought into a warm room.

Though neither of these theories has been proved to be true, and both of them have the merit of accounting for the phenomena of radiation, the preference is commonly given to the last. The theory of M. Prevost affords a more satisfactory explanation of the phenomena of radiant caloric than that of M. Pictet; but the chief argument in its favor is drawn from the close analogy between the laws of light and caloric. Luminous bodies certainly exchange rays with one another; a less intense light sends rays to one of greater intensity; and hence it may be inferred that an interchange of calorific rays takes place in a similar manner. Under this point of view, it is difficult to conceive how the radiation of one body should be influenced by the presence of another at a considerable distance from it.

This ingenious theory applies equally well to the experiments with the conjugate mirrors, as to the phenomena of ordinary radiation. If a metallic ball in the focus of one mirror, and a thermometer in that of the other, are both of the same temperature as the surrounding objects, (say at 60° F.) the thermometer remains stationary. It does indeed receive rays from the ball; but its temperature is not affected by them, because it gives back an equal number in return. If the ball is above 60° F. the thermometer begins to rise, because it now receives a greater number of rays than it gives out. If, on the contrary, the ball is below 60° F. then the thermometer, being the warmer of the two bodies, emits more rays than it receives, and its temperature falls.

The same mode of reasoning accounts very happily for an experiment originally performed by the Florentine Academicians, and since carefully repeated by M. Pictet, the result of which at first appeared quite anomalous. He placed a piece of ice instead of the metallic ball in the focus of his mirror, and observed that the thermometer in the opposite focus immediately descended, but rose again as soon as the ice was removed. On replacing the ice in the focus, the thermometer again fell, and reascended when it was withdrawn. It was supposed by some philosophers that this experiment proved the existence of frigorific rays, whose property was to communicate coldness; whereas, all the preceding remarks are made on the supposition that cold is merely a negative quality arising from the diminution of caloric. If, indeed, the result of M. Pictet's experiment could not be explained on the latter supposition, we should be obliged to adopt the former; but as we are not driven to that alternative, it is in nowise necessary to modify our views. In fact, as the thermometer gives more rays to the ice than it receives in return, it must necessarily become colder. It rises again when the ice is removed, because it then receives a number of calorific rays proceeding from the warmer surrounding objects, which were intercepted by the ice while it was in the focus. Whence it appears that the result of this experiment flows naturally out of M. Prevost's theory.*

* It flows no less naturally out of M. Pictet's views. In explaining the experiment of the apparent radiation of cold, it is necessary to distinguish two cases in which the equilibrium of temperature is dis-

A very elegant application of this theory was made by the late Dr Wells to account for the formation of dew*. The most copious deposition of dew takes place when the weather is clear and serene; and the substances that are covered with it are always colder than the contiguous strata of air, or than those bodies on which dew is not deposited. In fact, dew is a deposition of water previously existing in the air as vapour, and which loses its gaseous form only in consequence of being chilled by contact with colder bodies. In speculating, therefore, about the cause of this interesting and important phenomenon, the chief object is to discover the principle by which the reduction of temperature is effected. The explanation proposed by Dr Wells, and now almost universally adopted, is founded on the theory of M. Prevost. If it be admitted that bodies radiate at all times, their temperature can remain stationary only by their receiving from surrounding objects as many rays as they emit; and should a substance be so situated that its own radiation may continue uninterruptedly without an equivalent being returned to it, its temperature must necessarily fall. Such is believed to be the condition of the ground in a calm starlight evening. The calorific rays which are then

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turbed; 1st, by a body raised above the temperature of the surrounding medium; and 2d, by one below the temperature of such medium. If a thermometer, after being heated to the boiling point, be held in the air, it immediately commences to project its caloric into the surrounding colder medium. If, however, we hold a ball of snow near the bulb of a thermometer which has been standing in a temperate apartment, the mercury falls, not because the caloric is projected from the instrument, but rather because the caloric is drawn into the snow. The calorific tension of the space occupied by the snow is diminished, and the caloric of the surrounding medium is drawn in by what might be conveniently called calorific induction. The effect, at first, is felt in the immediate vicinity of the cold body and is thence propagated in right lines successively to greater and greater distances. If these views be admitted as probable, it will not be difficult to conceive how the direction of this motion of caloric by induction may be changed by the interposition of mirrors. There can be little doubt, that caloric constitutes a medium which pervades all space, and that rows of calorific particles in right lines must exist in every conceivable direction. In the experiment cited in the text, the ice in the focus of one mirror produces, by induction, a deficiency of caloric in its surface; a number of pre-existing rays are drawn into the ice, which are continuous with an equal number, parallel with the axis of the mirror. Let it be supposed that a particular row of particles is put in motion by induction, it is clear that a deficiency of caloric will be the consequence at some points on the surface of the mirror. This cannot be supplied by the mirror itself, and hence it will be made up by the first particle in the continuous parallel row. This produces an induction in the parallel row, which results in creating a deficiency of caloric in some point of the surface of the second mirror. Finally, a similar induction of caloric is created in the corresponding row of particles, leading to the focus of the second mirror where the thermometer is placed, which necessarily indicates a reduction of temperature. In this way we think the experiment of the radiation of cold may be explained, without the aid of M. Prevost's theory, which we conceive, on the whole, to be less simple than M. Pictet's views. B.

* Wells on Dew.

emitted by the substances on the surface of the earth are dispersed through free space and lost; nothing is present in the atmosphere to exchange rays with them, and their temperature consequently diminishes. If, on the contrary, the weather is cloudy, the radiant caloric proceeding from the earth is intercepted by the clouds, an interchange is established, and the ground retains nearly, if not quite, the same temperature as the adjacent portions of air.

All the facts hitherto observed concerning the formation of dew, tend to confirm this explanation. It is found that dew is deposited sparingly or not at all in cloudy weather; that all circumstances which promote free radiation are favourable to the formation of dew; that good radiators of caloric, such as grass, wood, the leaves of plants, and filamentous substances in general, reduce their temperature, in favourable states of the weather, to an extent of ten, twelve, or even fifteen degrees below that of the circumambient air; and that while these are drenched with dew, pieces of polished metal, smooth stones, and other imperfect radiators, are barely moistened, and are nearly as warm as the air in their vicinity.

## *On the Cooling of Bodies.*

It appears from the preceding remarks on the passage of caloric, that the cooling of bodies takes place by two very different methods. When a hot body is enveloped in solid substances, its caloric is withdrawn solely by means of communication, and the rapidity of cooling is dependent on the conducting power. The refrigeration is effected in a similar manner when the heated body is immersed in a liquid; but the rapidity of cooling depends partly on the conducting power of the liquid, and partly on the mobility of its particles. In elastic fluids the cooling takes place both by communication and radiation; and in a vacuum it is produced solely by radiation.

The first attempt to fix the rate of cooling was by Newton. He conceived that a hot body exposed to a uniform cause of refrigeration, as by exposure to the air, loses at each instant a quantity of caloric which always bears the same proportion to its excess. Thus if a hot body is deprived of 1-10th of its excess of caloric in one second, it should lose 1-10th of the remaining 9-10ths, or 9-100ths in the next second, and in the third second it will lose 1-10th of the remaining 81-100ths, or 81-1000ths, &c. In this way the following series of numbers may be obtained, expressing the proportion of the excess of caloric lost in equal intervals of time:—

$$\frac{1000}{10{,}000},\ \frac{900}{10{,}000},\ \frac{810}{10{,}000},\ \frac{729}{10{,}000},\ \frac{656}{10{,}000},\ \frac{590\cdot5}{10{,}000},\ \frac{531\cdot6}{10{,}000},\ \&c.$$

and the excess remaining after each interval is,

$$\frac{9000}{10{,}000},\ \frac{8100}{10{,}000},\ \frac{7290}{10{,}000},\ \frac{6560}{10{,}000},\ \frac{5905}{10{,}000}\ \frac{5316}{10{,}000},\ \&c.$$

It is obvious that the numerators of these fractions constitute a geometrical series, of which 1·111 is the ratio; for $5316\times1.111=5905$, $5316\times1{\cdot}111^2=6559$, $6316\times1{\cdot}111^3=7286$, &c. Hence it was inferred by Newton, that while the times of cooling are in arithmetical progression, the refrigeration proceeds according to a geometrical progression.

This subject has been experimentally investigated with remarkable ingenuity and success by MM. Dulong and Petit. (An. de Ch. et Ph. vii. 225.) They have demonstrated that Newton's law of refrige-

ration may be adopted when the temperature is inconsiderable; but that when a body cools through an extensive range of temperature, as when the excess of caloric is great, the law is then found to be erroneous. They have examined with consummate skill the various circumstances by which the cooling of a hot body in *vacuo*, or when surrounded by an elastic fluid, is influenced; but their inquiry is too mathematical and abstruse for the purposes of an elementary treatise.

## *Effects of Caloric.*

The phenomena that may be ascribed to the agency of caloric, and which may therefore be enumerated as its effects, are numerous. With respect to animals, it is the cause of the feelings of cold, agreeable warmth, and burning, according to its intensity. It excites the system powerfully, and without a certain degree of it the vital actions would entirely cease. Over the vegetable world its influence is obvious to every eye. By its stimulus co-operating with air and moisture, the seed bursts its envelope and yields a new plant, the buds open, the leaves expand, and the fruit arrives at maturity. With the declining temperature of the seasons, the circulation of the sap ceases, and the plant remains torpid till it is again excited by the stimulus of caloric.

The dimensions of every kind of matter are regulated by this principle. Its increase, with few exceptions, separates the particles of bodies to a greater distance from one another, producing expansion, so that the same quantity of matter is thus made to occupy a larger space; and the diminution of caloric has an opposite effect. Were the repulsion occasioned by this agent to cease entirely, the atoms of bodies would come into absolute contact.

The form of bodies is dependent on caloric. By its increase solids are converted into liquids, and liquids are dissipated in vapour; by its decrease vapours are condensed into liquids, and these become solid. Did matter cease to be under the influence of caloric, all liquids, vapours, and doubtless even gases, would become permanently solid; and all motion on the surface of the earth would be arrested.

When caloric is accumulated to a certain extent in bodies, they shine or become *incandescent*. On this important property depend all our methods of artificial illumination.

Caloric exerts a powerful influence over chemical phenomena. There is, indeed, scarcely any chemical action which is not in some degree modified by this principle; and hence a knowledge of the laws of caloric is indispensable to the chemist. By its means, bodies previously separate are made to combine, and the elements of compounds disunited. An undue proportion of it is destructive to all organic and many mineral compounds; and it is essentially concerned in combustion, a process so necessary to the wants and comforts of man.

Of the various effects of caloric above enumerated, several will be discussed in other parts of the work. In this place it is proposed to treat only of the influence of caloric over the dimensions and form of bodies; and this subject will be conveniently studied under the three heads of expansion, liquefaction, and vaporization.

## *Expansion.*

One of the most remarkable properties of caloric is the repulsion which

exists among its particles; hence it happens, that when this principle enters into a body, its first effect is to remove the integrant molecules of the substance to a greater distance from one another. The body therefore becomes less compact than before, occupies a greater space, or, in other words, expands. Now this effect of caloric is manifestly in opposition to cohesion—that force which tends to approximate the particles of matter, and which must be overcome before any expansion can ensue. It may be expected, therefore, that a small addition of caloric will occasion a small expansion, and a greater addition of caloric a greater expension; because in the last case, the cohesion will be more overcome than in the former. It may be anticipated, also, that whenever caloric passes out of a body, the cohesion being now left to act freely, a contraction will necessarily follow; so that expansion is only a transient effect, occasioned solely by the accumulation of caloric. It follows, moreover, from this view, that caloric must produce the greatest expansion in those bodies, whose cohesive power is least; and the inference is fully justified by observation. Thus the force of cohesion is greatest in solids, less in liquids, and least of all in aeriform substances; the expansion of solids is trifling, that of liquids much more considerable, and that of elastic fluids far greater.

It may be laid down as a rule, the reason of which is now obvious, that all bodies are expanded by caloric, and that the expansion of the same body increases with the quantity of caloric which enters it. But this law is a general one, only so long as the body under examination suffers no change in form or composition. If the caloric should produce one or both of these effects, then the reverse of expansion may ensue; not, however, as the direct consequence of an augmented temperature, but as the result of a change in form or composition.

In proof of the expansion of solids, we need only take the exact dimensions in length, breadth, and thickness of any substance when cold, and measure it again while strongly heated, when it will be found to have increased in every direction. A familiar demonstration of the fact may be afforded by adapting a ring to an iron rod, the former being just large enough to permit the latter to pass through it while cold. The rod is next heated, and will then no longer pass through the ring. This dilatation from heat and consequent contraction in cooling takes place with a force which appears to be irresistible.

The expansion of solids has engaged the attention of several experimenters, whose efforts have been chiefly directed towards ascertaining the exact quantity by which different substances are lengthened by a given increase of heat, and determining whether or not their expansion is equable at different temperatures. The Philosophical Transactions of London contain various dissertations on the subject by Ellicot, Smeaton, Troughton, and General Roy; and M. Biot in his *Traité de Physique*, has given the results of experiments performed with great care by Lavoisier and Laplace. Their experiments establish the following points: 1. Different solids do not expand to the same degree from equal additions of caloric. 2. A body which has been heated from the temperature of freezing to that of boiling water, and again allowed to cool to 32° F. recovers precisely the same volume which it possessed at first. 3. The dilatation of the more permanent or infusible solids is very uniform within certain limits; their expansion, for example, from the freezing point of water to 122° F. is equal to what takes place betwixt 122° and 212°. The subsequent researches of Dulong and Petit, (Annales de Ch. et de Ph. vol. vii.)

prove that solids do not dilate uniformly at high temperatures, but expand in an increasing ratio; that is, the higher the temperature beyond 212° F. the greater the expansion for equal additions of caloric. It is manifest, indeed, from their experiments, that the rate of expansion is an increasing one even between 32° and 212°; but the differences which exist within this small range are so inconsiderable as to escape observation, and therefore for all practical purposes may be disregarded.

The subjoined table includes the most interesting results of Lavoisier and Laplace. (Biot, vol. i. p. 158.)

| *Names of Substances.* | *Elongation when heated from 32 to 212°.* |
|---|---|
| Glass tube without lead, a mean of three specimens | 1-1115 of its length. |
| English flint glass | 1-1248 |
| Copper | 1-581 |
| Brass—mean of two specimens | 1-532 |
| Soft iron forged | 1-819 |
| Iron wire | 1-812 |
| Untempered steel | 1-927 |
| Tempered steel | 1-807 |
| Lead | 1-351 |
| Tin of India | 1-516 |
| Tin of Falmouth | 1-462 |
| Silver | 1-524 |
| Gold—mean of three specimens | 1-602 |
| Platinum, determined by Borda | 1-1167 |

Knowing the elongation of any substance for a given number of degrees of the thermometer, it is easy to calculate its total increase in bulk, by trebling the number which expresses its increase in length. Thus if a tube of flint glass elongates by 1-1248, when heated from the freezing to the boiling point of water, its cubic space will have increased by 3-1248 or 1-416 of its former capacity.

The expansion of glass, iron, copper and platinum, has been particularly investigated by MM. Dulong and Petit. The following table contains the result of their observations on glass. (An de Ch. et Ph. vii. 138.) It appears from the third column that at temperatures beyond 212° glass expands in a greater ratio than mercury.

| *Temperature by an air Thermometer.* | *Mean Absolute Dilatation of glass for each degree.* | *Temperature by a Thermometer made of glass.* |
|---|---|---|
| Fahr. | Fahr. | Fahr. |
| From 32° to 212° | 1-69660 | 212 |
| —— 32 to 392 | 1-65340 | 415.8 |
| —— 32 to 572 | 1-59220 | 667.2 |

The second, fourth and sixth columns of the following table show the mean total expansion of iron, copper and platinum, when heated from 32° to 212° and from 32° to 572°, for each degree. The third, fifth, and seventh columns indicate the degrees on a thermometer of iron, copper and platinum, corresponding to a temperature of 572° on an air thermometer. It is obvious that platinum is much more uniform in its expansion than either of the other metals.

| *Temp. by air thermometer.* | *Mean Dilat. of iron in volume for each deg.* | *Temperature by iron rod thermom.* | *Mean Dilat. of Copper in volume for each degree.* | *Temperature by Copper rod therm.* | *Mean Dilat. of Platinum in vol. for each degree.* | *Temperature by Platinum rod therm.* |
|---|---|---|---|---|---|---|
| Fahr. | Fahr. | Fahr. | Fahr. | Fahr. | Fahr. | Fahr. |
| 212° | 1-50760 | 212° | 1-34920 | 212° | 1-67860 | 212° |
| 572° | 1-40678 | 702.5 | 1-31860 | 623.8 | 1-65340 | 592.9 |

The simplest method of proving the expansion of liquids is by putting a common thermometer, made with mercury or alcohol, into warm water, when the dilatation of the liquid will be shown by its ascent in the stem. The experiment is indeed illustrative of two other facts. It proves, first, that the dilatation increases with the temperature; for if the thermometer is plunged into several portions of water heated to different degrees, the ascent will be greatest in the hottest water, and least in the coolest portions. It demonstrates, secondly, that liquids expand more than solids. The glass bulb of the thermometer is itself expanded by the hot water, and therefore is enabled to contain more mercury than before; but the mercury being dilated to a much greater extent, not only occupies the additional space in the bulb, but likewise rises in the stem. Its ascent marks the difference between its own dilatation and that of the glass, and is only the apparent, not the actual expansion of the liquid.

Different liquids do not expand to the same degree from an equal increase of temperature. Alcohol expands much more than water, and water than mercury. From the frequency with which the latter is employed in philosophical experiments, it is important to know the exact amount of its expansion. This subject has been investigated by several Philosophers, but the experiments of Lavoisier and Laplace, and especially of Dulong and Petit, from the extreme care with which they were made, are entitled to the greatest confidence. According to the former the actual dilatation of mercury, in passing from the freezing to the boiling point of water, amounts to 100-5412 of its volume, but the result obtained by Dulong and Petit, who found it 100-5550, is probably still nearer the truth. Adopting the last estimate, this metal dilates, for every degree of Fahrenheit's thermometer, 1-9990 of the bulk which it occupied at the temperature of 32°. If the barometer, for instance, stands at 30 inches when the thermometer is at 32°, we may calculate what its elevation ought to be when the latter is at 60°, or at any other temperature*. The apparent ex-

* The general formula is as follows: Let H be the height of the barometer when the thermometer is at 32° F.; H′ its elevation at any temperature above 32°, and let T express the number of degrees of Fahr. therm. above that point. Then $H'=H.\left(1+\frac{T}{9990}\right)$; hence $\frac{H'}{H}=1+\frac{T}{9990}$; $H'\,9990=H\,(9990+T)$; and $H'=H\,\frac{9990+T}{9990}$; or if H is unknown, it may be calculated by the formula $H=\frac{H'.9990}{9990+T}$. For H and T in the first formula substitute their value, as stated in the text, and perform the calculation. $H'=30.\frac{9990+28}{9990}=30{\cdot}084$. The

pansion of mercury contained in glass is of course less than the absolute expansion. Between the limits of 32° and 212° F. Lavoisier and Laplace estimate the apparent expansion at 1-63, and Dulong and Petit at 1-64.8 of its volume, being 1-11664 for each degree of Fahrenheit's thermometer. Dulong and Petit state that the mean total expansion of mercury from 32° to 572° F. for each degree is 1-9540; and that the mean apparent expansion in glass from 32° to 572° F. for every degree, is 1-11372. The temperature in their experiments was estimated by an air thermometer, which they consider more uniform in its rate of expansion than one of mercury. The temperature of 572° F. on the air thermometer corresponds to 586° in the mercurial one.

All experimenters agree that liquids expand in an increasing ratio, or that equal increments of caloric cause a greater dilatation at high than at low temperatures. Thus, if a fluid is heated from 32° to 122° it will not expand so much as it would do in being heated from 122° to 212°, though an equal number of degrees is added in both cases. In mercury the first expansion, according to Deluc, is to the second as 14 to 15; in olive oil as 13·4 to 15; in alcohol as 10·9 to 15; and in pure water as 4·7 to 15. Attempts have been made to discover a general law by which this progression is regulated, and Mr Dalton conceives that the expansion observes the ratio of the square of the temperature estimated from the point of congelation, or of greatest density; but this opinion is merely hypothetical, and has been shown by Dulong and Petit to be inconsistent with the facts established by their experiments.

There is a peculiarity in the effect of caloric upon the bulk of some fluids; namely, that at a certain temperature an increase of heat causes them to contract, and its diminution makes them expand. This singular exception to the general effect of caloric is only observable in those liquids which acquire an increase of bulk in passing from the liquid to the solid state, and is remarked only within a few degrees of temperature above their point of congelation. Water is a noted example of it. Ice, as every one knows, swims upon the surface of water, and therefore must be lighter than it, which is a convincing proof that water, at the moment of freezing, must expand. The increase is estimated by Boyle at about 1-9th of its volume. (Experiments on cold.)

The most remarkable circumstance attending this expansion, is the prodigious force with which it is effected. Mr Boyle filled a brass tube, three inches in diameter, with water, and confined it by means of a moveable plug; the expansion, when it froze, took place with such violence as to push out the plug, though preserved in its situation by a weight equal to 74 pounds. The Florentine Academicians burst a hollow brass globe, whose cavity was only an inch in diameter, by freezing the water with which it was filled; and it has been estimated that the expansive power necessary to produce such an effect was equal to a pressure of 27,720 pounds weight. Major Williams gave ample confirmation of the same fact by some experiments which he performed at Quebec in the years 1784 and 1785. (Philosophical Transactions of Ed. ii. 23.)

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rate of actual and not apparent expansion is employed in this calculation, because the length of the mercurial column, being determined by the atmospheric pressure, is not affected by the expansion or contraction of the tube.

But it is not merely during the act of congelation that water expands; for it begins to dilate considerably before it actually freezes. Dr Croune noticed this phenomenon so early as the year 1683, and it has since been observed by various philosophers. It may be rendered obvious to any one by the following experiment. Fill a flask, capable of holding three or four ounces, with water at the temperature of 60° F. and adapt to it a cork, through which passes a glass tube open at both ends, about the eighth of an inch wide, and ten inches long. After having filled the flask, insert the cork and tube, and pour a little water into the latter till the liquid rises to the middle of it. On immersing the flask into a mixture of pounded ice and salt, the water will fall in the tube, marking contraction; but in a short time an opposite movement will be perceived, indicating that dilatation is taking place, while the water within the flask is at the same time yielding caloric to the freezing mixture in which it is immersed.

To the inference deduced from this experiment it was objected by some philosophers, that the ascent of the water in the tube did not arise from any expansion in the liquid itself, but from a contraction of the flask, by which its capacity was diminished. In fact, this cause does operate to a certain extent, but is by no means sufficient to account for the whole effect; and, accordingly, it has been proved by an elegant and decisive experiment of Dr Hope, that water does really expand previous to congelation*. He believes the greatest density of water to be between thirty-nine and a half and forty degrees of Fahrenheit's thermometer; that is, boiling water obeys the usual law till it has cooled to the temperature of about 40° F. after which the abstraction of caloric produces an increase instead of a diminution of volume. According to M. Hallström, whose experiments are the most recent, and appear to have been conducted with great care, the maximum density of water is 39°.39 F. (An. de Ch. et Ph. xxviii. 90.)

The cause of the expansion of water at the moment of freezing is attributed to a new and peculiar arrangement of its particles. Ice is in reality crystallized water, and during its formation the particles arrange themselves in ranks and lines, which cross each other at angles of 60° and 120°, and consequently occupy more space than when liquid. This may be seen by examining the surface of water while freezing in a saucer. No very satisfactory reason can be assigned for the expansion which takes place previous to congelation. It is supposed, indeed, that the water begins to arrange itself in the order it will assume in the solid state before actually laying aside the liquid form; and this explanation is generally admitted, not so much because it has been proved to be true, but because no better one has been offered.

Water is not the only liquid which expands under reduction of temperature, as it is observed in a few others which assume a highly crystalline structure on becoming solid;—fused iron, antimony, zinc, and bismuth, are examples of it. Mercury is a remarkable instance of the reverse; for when it freezes, it suffers a very great contraction.

As the particles of air and aeriform substances are not held together by cohesion, it follows that increase of temperature must occasion a considerable dilatation of them; and, accordingly, they are found to dilate from equal additions of caloric much more than solids or liquids. Now, chemists are in the habit of estimating the quantity of the gases employed in their experiments by measuring them, and since the volume occupied by any gas is so much influenced by temperature, it is es-

* Philosophical Transactions of Edinburgh, v. 379.

sential to accuracy that a due correction be made for the variations arising from this cause; that they should know how much dilatation is produced by each degree of the thermometer, whether the rate of expansion is uniform at all temperatures, and whether that ratio is the same in all gases.

This subject had been unsuccessfully investigated by several philosophers, who failed in their object chiefly because they neglected the precaution of drying the gases upon which they operated; but at last the law of dilatation was detected by Dalton and Gay-Lussac nearly at the same time. Mr Dalton's method of operating (Manchester Memoirs, vol. v.) was exceedingly simple. He filled with dry mercury a graduated tube, closed at one end and carefully dried; and then plunging the open end of the tube into a mercurial trough, introduced a portion of dry air. After having marked the bulk and temperature of the air, he exposed it to a gradually increasing heat, the exact amount of which was regulated by a thermometer, and observed the dilatation occasioned by each increase of temperature. The apparatus of M. Gay-Lussac (An. de Chimie, v. 43.) was the same in principle, but more complicated, in consequence of the precautions he took to avoid every possible source of fallacy.

It is proved by the researches of these philosophers, that all gases undergo equal expansions by the same addition of caloric, supposing them placed under the same circumstances; so that it is sufficient to ascertain the law of expansion observed by any one gas, in order to know the law for all. Now it appears from the experiments of Gay-Lussac, that 100 parts of air in being heated from 32° to 212° F. expand to 137·5 parts. The increase for 180 degrees is therefore 0·375 or 37·5-100th of its bulk; and by dividing this number by 180, it is found that a given quantity of dry air dilates to 1-480th of the volume it occupied at 32°, for every degree of Fahrenheit's thermometer. The result of Dalton's experiments corresponds very nearly with the foregoing.

This point being established, it is easy to ascertain what volume any given quantity of gas should occupy at any given temperature. Suppose a certain portion of gas occupies 20 measures of a graduated tube at 32°, it may be desirable to determine what would be its bulk at 42° F. For every degree of heat it has increased by 1-480th of its original volume, and therefore, since the increase amounts to ten degrees, the 20 measures will have dilated by 10-480ths. The expression will therefore be $20+20\times 10\text{-}480=20{\cdot}416$. It must not be forgotten that the volume which the gas occupies at 32° is a necessary element in all such calculations. Thus, having 20·416 measures of gas at 42° F. the corresponding bulk for 52° F. cannot be calculated by the formula $20{\cdot}416+20{\cdot}416\times 10\text{-}480$; the real expression is $20.416+20\times 10\text{-}480$; because the increase is only 10-480ths of the space occupied at 32° F. which is 20 measures.* A similar remark

* Very convenient general formulæ for such calculations may be thus deduced: let P′ be the volume of gas at any temperature above 32°, T the number of degrees above that point, and P its volume at 32°. Then, $P' = \left(1+\frac{T}{480}\right)$; hence $\frac{P'}{P} = 1+\frac{T}{480}$; $P'\,480 = P\,(480+T)$; and $P' = P\,\frac{(480+T)}{80}$.

Or if P is unknown, it may be calculated by the formula $P = \frac{P'\,480}{480+T}$.

applies to the formula for estimating the effect of heat on the height of the barometer.

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It frequently happens, in the employment of Fahrenheit's thermometer, that when P′ for the above formula is known, it is not P itself which is wanted, but the volume of gas at some other temperature, as at 60° F. This value may be obtained without first calculating what P is. Let P′, for instance, be any known quantity of gas at a certain temperature; and let P″ be the quantity sought at some other temperature, the degrees of which above 32° may be expressed by T′. Now $P'' = \frac{(480+T')}{480} \times P$; but as P is unknown, let its value be substituted according to the above formula. Thus, $P'' = \left(\frac{480+T'}{480}\right) \times \left(\frac{P'\,480}{480+T}\right)$; which gives $P'' = \frac{480^2 P' + 480\ T' P'}{480^2 + 480\ T} = \frac{P'\,480}{480} \frac{(480+T')}{(480+T)} = \frac{P'(480+T')}{480+T}$.

Suppose, for example, a portion of gas occupies 100 divisions of a graduated tube at 48° F, how many will it fill at 60° F? Here P′ = 100; T = 48—32 or 16; T′ = 60—32, or 28. The number sought, or the $P'' = \frac{100 \times 508}{496} = 102.42$*.

* To those who are not algebraists, the following explanation and calculation may be useful. As every gas expands 1-480th of the volume it would occupy at 32°, for every degree of Fahrenheit's thermometer, it is clear that it will expand 1-481st part of its volume at 33°, 1-482nd part of its volume at 34°, and so on for each successive addition of one degree of caloric. In order to know, therefore, the fractional dilatation of a gas at any temperature above 32°, for a single degree, it is only necessary to add to the numerator of the fraction 1-480, a number of units equal to the number of degrees that the gas exceeds the temperature of 32°. Thus a gas at the temperature of 42° will expand 1-490th, at 52° 1-500, of its volume, by every increment of heat equal to one degree. Knowing in this simple manner the fractional amount of expansion of a gas at any temperature for one degree, we multiply this amount by the difference between the existing temperature and the temperature to which it is desired to reduce the volume. If the reduction is to a higher temperature, this product is added to the existing volume; if to a lower, subtracted. Thus, to calculate the example which Dr Turner has selected, namely, 100 measures of a gas at 48°, what will be its bulk at 60°? we proceed as follows: as the existing temperature is 16° above 32°, its fractional expansion for one degree will be 1-480+16 or 1-496. Taking the 496th part of one hundred, the given volume, we have the actual expansion for one degree. This, upon calculation, will be found to be .2016, which multiplied by 12, the difference between the actual temperature and the temperature of the volume sought, will give 2·419, as the actual expansion, corresponding to 12 degrees. As the temperature of the volume sought is above the original temperature, this number must be added to the given volume. So that 100+2·419=102·419 will be the volume sought. B.

The rate of expansion of atmospheric air at temperatures exceeding 212° has been examined by MM. Dulong and Petit, and the following Table contains the result of their observations. (*An. de Ch. et Ph.* vii. 120.)

| Temperature by the Mercurial Thermometer. Fahrenheit. | Temperature by the Mercurial Thermometer. Centigrade. | Corresponding volumes of a given volume of air. |
|---|---|---|
| — 33 | — 36 .. | 0.8650 |
| 32 | 0 .. | 1.0000 |
| 212 | 100 .. | 1.3750 |
| 302 | 150 .. | 1.5576 |
| 392 | 200 .. | 1.7389 |
| 482 | 250 .. | 1 9189 |
| 572 | 300 .. | 2.0976 |
| Mercury boils 680 | 360 .. | 2.3125 |

Hydrogen gas was found to expand in the same proportion, so that all gases may be inferred to expand to the same extent for equal increments of caloric between —33° F. and 680°; and in all probability the same law prevails at all temperatures.*

## *On the Thermometer.*

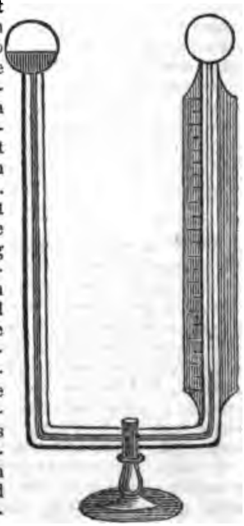
The influence of caloric over the bulk of bodies is better fitted for estimating a change in the quantity of that agent than any other of its properties; for substances not only expand more and more as the temperature increases, but return exactly to their original volume when the heat is withdrawn.† The first attempt to measure the intensity of heat on this principle was made early in the seventeenth century, and the honour of the invention is by some bestowed on Sanctorius, by others on Cornelius Drebel, and by others on the celebrated Galileo. The material used by Sanctorius was atmospheric air. The construction of the thermometer itself, or *thermoscope* as it was sometimes called, is exceedingly simple. A glass tube is to be

* The law of the equable expansion or contraction of gases by equal increments or decrements of heat is a very curious one, but becomes particularly so when viewed in connection with a descending temperature. If gases expand or contract 1-480th of the volume they occupy at the freezing point, for every alteration of temperature equal to one degree, it is obvious that a given volume of any gas at 32° will be *expanded* by a volume equal to itself, by having its temperature raised 480°. But the converse of the proposition would seem to involve a paradox; for by the application of the same law, a given volume of any gas at 32°, if cooled down 480°, would be *contracted* by a volume equal to itself, that is, reduced to nothing. B.

† Some experiments made by Dr Ure seem to invalidate the universality of the law, that bodies after being heated return exactly to their original volume, when the heat is withdrawn. Dr Ure, upon making some experiments on rods of zinc, found that they were permanently elongated after having been first heated and then cooled. He supposes "that the plates composing this metal, in sliding over each other by the expansive force of heat, present such an adhesive friction as to prevent their entire retraction." *Ure's Dictionary.* B.

selected for the purpose, and one end of it is blown out into a spherical cavity, while its other extremity is left open. After expelling a small quantity of air by heating the ball gently, the open end of the tube is plunged into coloured water, and a portion of the liquid is forced up into the tube by the pressure of the atmosphere, as the air within the ball contracts. In this state it marks changes of temperature with extreme delicacy, the alternate expansion and contraction of the confined air being rendered visible by the corresponding descent and ascent of the coloured water in the stem; and in point of sensibility, indeed, it yields to no instrument. The material used in its construction, also, is peculiarly appropriate, because air, like all gases, expands uniformly by equal increments of caloric; but, nevertheless, independently of these advantages, there are two forcible objections to the employment of this thermometer. For, in the first place, its dilatations and contractions are so great, that it will be inconvenient to measure them when the change of temperature is considerable; and, secondly, its movements are influenced by pressure as well as by caloric, so that the instrument would be affected by variations of the barometer, though the temperature should be quite stationary.

For the reasons just stated, the common air thermometer is rarely employed; but a modification of it, described in 1804 by Professor Leslie in his Essay on Heat, under the name of *Differential Thermometer*, is entirely free from the last objection, and is admirably fitted for some special purposes. This instrument was invented a century and a half ago by Sturmius, Professor of Mathematics at Altdorff, who has left a description and sketch of it in his *Collegium Curiosum*, p. 54, published in the year 1676; but like other air thermometers it had fallen into disuse, till it was again brought into notice by Professor Leslie. As now made it consists of two thin glass balls joined together by a tube, bent twice at a right angle, as represented in the annexed figure. Both balls contain air, but the greater part of the tube is filled with sulphuric acid coloured with carmine. It is obvious that this instrument cannot be affected by any change of temperature acting equally on both balls; for as long as the air within them expands or contracts to the same extent, the pressure on the opposite surfaces of the liquid, and consequently its position, will continue unchanged. Hence the differential thermometer stands at the same point, however different may be the temperature of the medium. But the slightest difference between the temperature of the two balls will instantly be detected; for the elasticity of the air on one side being then greater than that on the other, the liquid will retreat towards the ball whose temperature is lowest.



Solid substances are not better suited to the construction of a thermometer than gases; for while the expansion of the latter is too great, that of the former is so small that it cannot be measured except by the adaptation of complicated machinery. Liquids which expand more than the one and less than the other, are exempt from both extremes;

and, consequently, we must search there for a material with which to construct a thermometer. The principle of selection is plain. A material is required whose expansions are uniform, and whose boiling and freezing points are very remote from one another. Mercury fulfils these conditions better than any other liquid. No fluid can support a greater degree of heat without boiling than mercury, and none, except alcohol and ether, can endure a more intense cold without freezing. It has, besides, the additional advantage of being more sensible to the action of caloric than other liquids, while its dilatations between 32° and 212° are almost perfectly uniform. Strictly speaking, the same quantity of caloric does occasion a greater dilatation at high than at low temperatures, so that, like other fluids, it expands in an increasing ratio. But it is remarkable that this ratio, within the limits assigned, is exactly the same as that of glass; and therefore, if contained in a glass tube, the increasing expansion of the vessel compensates for that of the mercury.

The first object in constructing a thermometer is to select a tube with a very small bore, which is of the same diameter through its whole length; and then, by melting the glass, to blow a small ball at one end of it. The mercury is introduced by rarefying the air within the ball, and then dipping the open end of the tube into that liquid. As the air cools and contracts, the mercury is forced up, entering the bulb to supply the place of the air which had been expelled from it. Only a part of the air, however, is removed by this means; the remainder is driven out by the ebullition of the mercury.

Having thus contrived that the bulb and about one-third of the tube shall be full of mercury, the next step is to seal the open end hermetically. This is done by heating the bulb till the mercury rises very near the summit, and then suddenly darting a fine pointed flame from a blow-pipe across the opening, so as to fuse the glass and close the aperture before the mercury has had time to recede from it.

The construction of a thermometer is now so far complete that it affords a means of ascertaining the comparative temperature of bodies; but it is deficient in one essential point, namely, the observations made with different instruments cannot be compared together. To effect this object, the thermometer must be graduated, a process which consists of two parts. The first and most important, is to obtain two fixed points which shall be the same in every thermometer. The practice now generally followed for this purpose was introduced by Sir Isaac Newton, and is founded on the fact, that when a thermometer is plunged into ice that is dissolving, or into water that is boiling, it constantly stands at the same elevations in all countries, provided there is a certain conformity of circumstances. The point of congelation is easily determined. The instrument is to be immersed in snow or pounded ice, which is liquefying in a moderately warm atmosphere, till the mercury becomes stationary. To fix the boiling point is a more delicate operation, since the temperature at which water boils is affected by various circumstances, which will be more particularly mentioned hereafter. It is sufficient to state the general directions at present;—that the water be perfectly pure, free from any foreign particles, and not above an inch in depth,—the ebullition brisk, and conducted in a deep metallic vessel, so that the stem of the thermometer may be surrounded by an atmosphere of steam, and thus exposed to the same temperature as the bulb,—the vapour be allowed to escape freely,—and the barometer stand at 30 inches.

The second part of the process of graduation consists in dividing the interval between the freezing and boiling points of water, into any

number of equal parts or degrees, which may be either marked on the tube itself, by means of a diamond, or first drawn upon a piece of paper, ivory or metal, and afterwards attached to the thermometer. The exact number of degrees into which the space is divided, is not very material, though it would be more convenient did all thermometers correspond in this respect. Unfortunately this is not the case. In Britain we use Fahrenheit's scale, while the continental philosophers employ either the centigrade, or that of Reaumur. The centigrade is the most convenient in practice; its boiling point is 100, that of melting snow is the zero, or beginning of the scale, and the interval is divided into 100 equal parts. The interval in the scale of Reaumur is divided into 80 parts, and in that of Fahrenheit into 180; but the zero of Fahrenheit is placed 32 degrees below the temperature of melting snow, and on this account the point of ebullition is 212°.

It is easy to reduce the temperature expressed by one thermometer to that of another, by knowing the relation which exists between their degrees. Thus, 180 is to 100 as 9 to 5, and to 80 as 9 to 4; so that nine degrees of Fahrenheit are equal to five of the centigrade, and four of Reaumur's thermometer. Fahrenheit's is therefore reduced to the centigrade scale, by multiplying by five, and dividing by nine, or to that of Reaumur, by multiplying by four instead of five. Either of these may be reduced to Fahrenheit by reversing the process; the multiplier is nine in both cases, and the divisor four in the one and five in the other. But it must be remembered in these reductions, that the zero of Fahrenheit's thermometer is 32 degrees lower than that of the centigrade or Reaumur, and a due allowance must be made for this circumstance. An example will best show how this is done. To reduce 212° F. to the centigrade, first abstract 32, which leaves 180; and this number multiplied by 5-9, gives the corresponding expression in the centigrade scale. Or to reduce 100° C. to Fahrenheit, multiply by 9-5, and then add 32. To save the trouble of such reductions, I have subjoined a table, which shows the degrees on the centigrade scale, and that of Reaumur corresponding to the degrees of Fahrenheit's thermometer.

| *Fahrenheit.* | *Centigrade.* | *Reaumur.* |
|---|---|---|
| 212 | 100 | 80 |
| 200 | 93·33 | 74·66 |
| 190 | 87·77 | 70·22 |
| 180 | 82·22 | 65·77 |
| 170 | 76·66 | 61·33 |
| 160 | 71·11 | 56·88 |
| 150 | 65·55 | 52·44 |
| 140 | 60 | 48 |
| 130 | 54·44 | 43·55 |
| 120 | 48·88 | 39·11 |
| 110 | 43·33 | 34·66 |
| 100 | 37·77 | 30·22 |
| 90 | 32·22 | 25·77 |
| 80 | 26·66 | 21·33 |
| 70 | 21·11 | 16·88 |
| 60 | 15·55 | 12·44 |
| 50 | 10 | 8 |
| 40 | 4.44 | 3·55 |
| 32 | 0 | 0 |
| 20 | — 6·66 | — 5·33 |
| 10 | —12·22 | — 9·77 |
| 0 | —17·77 | —14·22 |

The mercurial thermometer may be made to indicate temperatures which exceed 212°, or fall below zero, by continuing the degrees above and below those points. But as mercury freezes at 39 degrees below zero, it cannot indicate temperatures below that point; and indeed the only liquid which can be used for such purposes is alcohol. Our means of estimating high degrees of heat are as yet very unsatisfactory. Mercury is preferable to any other liquid; but even its indications cannot be altogether relied on. For, in the first place, its expansion for equal increments of caloric is greater at high than at low temperatures; and secondly, glass expands at temperatures beyond 212° F. in a more rapid ratio than mercury, and consequently, from the proportionally greater capacity of the bulb, the apparent expansion of the metal is considerably less than its actual dilatation. Thus MM. Dulong and Petit observed, that when the air thermometer is at 572° F. the common mercurial thermometer stands at 586°; but when corrected for the error caused by the glass, it indicates a temperature of 597.5° F. No liquid can be employed for temperatures which exceed 180° F. since all of them are then either dissipated in vapour or decomposed.

The instruments for measuring intense degrees of heat are called *pyrometers*, and must be formed either of solid or gaseous substances. The former alone have been hitherto employed, though the latter, from the greater uniformity with which they expand, are better calculated for the purpose. The pyrometer invented by Mr Wedgwood is best known. It is founded on the property which clay possesses of contracting, when strongly heated, without returning to its former dimensions as it cools. The earth alumina, whether precipitated from a solution by reagents, or found more or less pure in the earth as clay, is always in a state of chemical combination with water. On heating it to redness, a part of the water is expelled; but some remains, which requires a very strong heat before it is dissipated; and in proportion as these last portions escape, the earth contracts. The contraction even continues after every trace of water has been removed, owing to a partial vitrification taking place, which tends to bring the particles of the clay into nearer proximity. The intensity of the heat may, therefore, in some measure be estimated by the degree of contraction which it has occasioned.

The apparatus consists of a metallic groove, 24 inches long, the sides of which converge, being half an inch wide above, and three-tenths below. The clay, well washed, is made up into little cubes* that fit the commencement of the groove, after having been heated to redness; and their subsequent contraction by heat is determined by allowing them to slide from the top of the groove downwards, till they arrive at a part of it through which they cannot pass. Mr Wedgwood divides the whole length of the groove into 240 degrees, each of which he supposes equal to 130° F. The zero of his scale corresponds to the 1077th degree of Fahrenheit.

Wedgwood's pyrometer is rarely employed at present, because its indications cannot be relied on. Every observation requires a separate piece of clay, and the observer is never sure that the contraction of the second cube, from the same heat, will be exactly similar to that of the first; especially as it is difficult to procure specimens of the earth whose composition is in every respect the same.

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* In this statement, Dr Turner is slightly inaccurate; for strictly speaking the pieces of clay are little *cylinders*, flattened on one side. B.

Other pyrometers have been proposed, which act on the usual principle of dilatation. They consist of a metallic bar, the elongation of which from heat is rendered sensible by an index being attached to one end, while the other is fixed. The experiments of Lavoisier and Laplace on the expansion of solids were made with such an apparatus, and Mr Daniell has lately described a similar one in the 11th volume of the Quarterly Journal of Science. These instruments are in general too complicated for common use; and, moreover, scientific men have hitherto placed little confidence in them, in consequence of the irregularity with which solids expand at high temperatures.

For some purposes, especially in making meteorological observations, it is a very desirable object to ascertain the highest and lowest temperature which has occurred in a given interval of time, during the absence of the observer. The instrument employed with this intention is called a *Register Thermometer*, and the most convenient kind with which I am acquainted, is that described in the Philosophical Transactions of Edinburgh, iii. 245, by Dr John Rutherford. The thermometer for ascertaining the most intense cold is made with alcohol, and the bulb is bent at a right angle to the stem, so that the latter may conveniently be placed in a horizontal position. In the spirit is immersed a cylindrical piece of black enamel, of such size as to move freely within the tube. In order to make an observation, the enamel should be brought down to the surface of the spirit, an object easily effected by slight percussion while the bulb is inclined upwards. When the thermometer sinks by exposure to cold, the enamel likewise retreats towards the bulb, owing to its adhesion to the spirit; but, on expanding, the spirit passes readily beyond the enamel, leaving it at the extreme point to which it had been conveyed by the previous contraction.

For registering the highest temperature, a common mercurial thermometer of the same form as the preceding is employed, having a small cylindrical piece of black enamel at the surface of the mercury. When the mercury expands, the enamel is pushed forward; and as the stem of the thermometer is placed horizontal, it does not recede when the mercury contracts, but remains at the spot to which it had been conveyed by the previous dilatation. The enamel is easily restored to the surface of the mercury by slight percussion while the bulb is inclined downwards; but this should be performed with care, lest the enamel, in falling abruptly, should interrupt the continuity of the mercurial column, and destroy the instrument. This accident is prevented by putting some pure naphtha in the tube beyond the mercury, and its presence is likewise of use in preventing the oxidation of the mercury.—The above description applies to an improvement on Dr Rutherford's thermometer made by Mr Adie of Edinburgh.

Though the thermometer is one of the most valuable instruments of philosophical research, it must be confessed that the sum of information which it conveys is very small. It does indeed point out a difference in the temperature of two or more substances with great nicety; but it does not indicate how much caloric any body contains. It does not follow, because the thermometer stands at the same elevation in any two bodies, that they contain equal quantities of caloric; nor is it right to infer that the warmer possesses more of this principle than the colder. The thermometer gives the same kind of information which may be discovered, though less accurately, by the feelings; it recognises in bodies that state of the caloric alone which affects the senses with an impression of heat or cold; the condition expressed by the word *temperature*. All we learn by this instrument, is whether

the temperature of one body is greater or less than that of another; and if there is a difference, it is expressed numerically, namely, by the degrees of the thermometer. But it must be remembered that these degrees are parts of an arbitrary scale, selected for convenience, without any reference whatever to the actual quantity of caloric present in bodies.

Very little reflection will evince the propriety of these remarks. If two glasses of unequal size be filled with water just taken from the same spring, the thermometer will stand in each at the same height, though their quantities of caloric are certainly unequal. This observation naturally gives rise to an interesting question; namely, do different kinds of substances, whose temperatures as estimated by the thermometer are the same, contain equal quantities of caloric? For example, does a pound of iron contain as much caloric as a pound of water, or of mercury? The foregoing remark shows that equality of temperature is not necessarily connected with equality in the quantity of caloric; and this inference has been amply confirmed by experiment. If equal quantities of water are mixed together, one portion being at 100° F. and the other at 50°, the mixture will have a temperature of 75°, or intermediate between the two; that is, the 25 degrees which the warm water has lost, have just sufficed to raise the cold water by as many degrees. It is hence inferred that equal weights of water of the same temperature contain equal quantities of caloric; and the same is found to be true of other bodies. But if equal weights, or equal bulks of different substances are used in the experiment, the result will be very different. Thus, if one pound of mercury at 185° F. is mixed with a pound of water at 40°, the mixture will have a temperature of 45° only; or if the experiment be reversed by having the water at 185° and the mercury at 40°, the mixture will have a temperature of 180°. In the first case, 140 degrees lost by the mercury served to heat the water by five degrees, and in the second, five degrees lost by the water sufficed to raise the temperature of the mercury by 140°. It hence appears that 28 times more caloric is required to raise the temperature of water through one or more degrees, than for heating an equal weight of mercury to the same extent; and if the same relation exist throughout the whole range of temperature, commencing from the absolute zero, then it would follow that the former contains 28 times more caloric than the latter.

Similar experiments have been made by mixing water with a great many other substances; and it is observed that different bodies always require unequal quantities of caloric to heat them equally. The same quantity of caloric which heats a pound of water one degree, will heat an equal weight of spermaceti oil two degrees, and, therefore, water is supposed to contain twice as much caloric as oil.

Dr Black was the first who noticed this remarkable difference, and he expressed it by the term *capacity* for caloric*. This word was probably suggested by the idea that the capacity of a body for caloric depends upon its capaciousness, or the distance between its particles, in consequence of which there is more room for caloric. And indeed at first view there appear sufficient grounds for this opinion; for it is observed, that very compact bodies have the smallest capacities for caloric, and that the capacity of the same substance often increases as its density becomes less. But, as Dr Black himself pointed out, if this was the real cause of the difference, the capacity of bodies for

* Black's Lectures.

caloric should be inversely as their density. Thus, since mercury is thirteen times and a half denser than water, the capacity of the latter for caloric ought to be only thirteen times and a half greater than the former, whereas it is twenty-eight times as great. Oil occupies more space than an equal weight of water, and yet the capacity of the latter for caloric is double that of the former. The word capacity therefore is apt to excite a wrong notion, unless it is carefully borne in mind, that it is merely an expression of the fact without allusion to its cause; and to avoid the chance of error from this source, the term *specific caloric* has been proposed as a substitute for it, and is now very generally employed.

It is certainly a singular fact, that two substances of equal temperature should contain unequal quantities of caloric, and many attempts have been made to account for it. The explanation deduced from the views of Dr Black is the following: He conceived that caloric exists in bodies under two opposite conditions; in one it is supposed to be in a state of chemical combination, when it lays aside its prominent characters, and remains as it were concealed, without evincing any signs of its presence; in the other, it is free and uncombined, passing readily from one substance to another, affecting the senses in its passage, determining the height of the thermometer, and in a word giving rise to all the phemomena which are attributed to this active principle.

Objections might easily be started against this ingenious conjecture; but it certainly has the merit of explaining phenomena more satisfactorily than any view that has been proposed in its place. It is entirely consistent with analogy. For since caloric is regarded as a material substance, it would be altogether anomalous were it not influenced, like other kinds of matter, by chemical affinity; and if this be admitted, it ought certainly, in combining, to lose some of the properties by which it is distinguished in its free state. According to this view, it is intelligible how two substances, from being in the same condition with respect to free caloric, may have the same temperature; and yet that their actual quantities of caloric may be very different, in consequence of one containing more of that principle in a combined or latent state than the other. But in admitting the plausibility of this explanation, it is proper to remember that it is at present entirely hypothetical; and that the language suggested by an hypothesis should not be unnecessarily associated with the phenomena to which it owes its origin. Accordingly, the word *sensible* is better than *free* caloric, and *insensible* preferable to *combined* or *latent* caloric; for by such terms the fact is equally well expressed, and philosophical propriety strictly preserved*.

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* The theory of latent heat of Dr Black, as applied to the explanation of the different specific heats of bodies, would seem in some respects to be unphilosophical. If Pictet's theory of the equilibrium of caloric be admitted, then the equality of temperature of any two bodies means merely that their caloric has no tendency to pass from one to the other, without the idea having any necessary connection with the absolute quantity of caloric contained in them. It may be admitted as highly probable that the reason why different bodies assume to themselves unequal quantities of heat, when this principle has assumed a state of rest, is that their affinities for caloric are different; yet it by no means follows, that the caloric in such bodies is in

It is of importance to know the specific caloric of bodies. The most convenient method of discovering it, is by mixing different substances together in the way just described, and observing the relative quantities of caloric requisite for heating them by the same number of degrees. The caloric required to heat equal quantities of water, spermaceti oil, and mercury by one degree, is in the ratio of 28, 14, and 1, and therefore their capacities for caloric are expressed by those numbers. Water is commonly one of the materials employed in such experiments, as it is customary to compare the capacity of other bodies with that of water.

This method was first suggested by Dr Black, and was afterwards practised to a great extent by Drs Crawford and Irvine*. But the same knowledge may be obtained by reversing the process,—by noting the relative quantities of caloric which bodies give out in cooling; for if water requires 28 times more caloric than mercury to raise its temperature by one or more degrees, it must also lose 28 times as much when it cools. The calorimeter, invented and employed by Lavoisier and Laplace, acts on this principle. The apparatus consists of a wire cage, suspended in the centre of a metallic vessel so much larger than itself, that an interval is left between them, which is filled with fragments of ice. The mode of estimating the quantity of caloric which is emitted by a hot body placed in the wire cage, depends upon the fact, that ice cannot be heated beyond 32° F; since every particle of caloric which is then supplied is employed in liquefying it, without in

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two different states, *sensible* or *free*, and *insensible* or *combined*. If we impart ten degrees of heat to equal weights of water and oil, the water will have received twice as much caloric as the oil. Here "the actual quantities of caloric" received are " very different;" but are we on this account to suppose that part of the caloric received by the water is in an insensible or combined state? It will at once be evident that this cannot be the case; for if the equal weights of water and oil, after being heated ten degrees, be allowed to cool equally, the water will lose twice as much actual caloric as the oil. Now all the caloric lost during the cooling becomes free caloric; for it is distributed among surrounding bodies.

The fact is, that the quantity of caloric gained or lost by any number of bodies, in being heated or cooled through the same number of degrees, bears a constant proportion to their several specific heats. Hence to maintain an equality of temperature among any set of bodies, the quantity of caloric contained by each must be directly proportional to its specific heat. Whatever *subverts* this relation will necessarily change the temperature.

It sometimes happens that the loss or gain of caloric by a body is exactly proportional to the change it may undergo in specific heat or capacity. Thus, if a body receive caloric, and have, at the same time, its capacity proportionably increased, its temperature remains the same, though it be constantly receiving caloric; and it is by such cases as these that the doctrine of insensible or combined heat is most plausibly supported. But, upon taking a nearer view of the subject, it will be found that the temperature remains the same in conformity with the principles laid down in this note; for the capacity and heat being simultaneously and proportionably increased, the relation between them, so far from being *subverted*, is maintained. B.

* Crawford on Animal Heat, and Irvine's Chemical Essays.

the least affecting its temperature. If, therefore, a flask of boiling water is put into the cage, it will gradually cool, the ice will continue at 32°, and a portion of ice-cold water will be formed; and the same change will happen when heated mercury, oil, or any other substance is substituted for the hot water. The sole difference will consist in the quantity of ice liquefied, which will be proportional to the caloric lost by those bodies while they cool; so that their capacity is determined merely by measuring the quantity of water produced by each of them. This is done by allowing the water, as it forms, to run out of the calorimeter by a tube fixed in the bottom of it, and carefully weighing the liquid which issues.

There is one obvious source of fallacy in this mode of operating, against which it is necessary to provide a remedy; namely, the ice not only receives caloric from the substance in the central cage, but must also receive it from the air of the apartment in which the experiment is conducted. This inconvenience is completely avoided by surrounding the whole apparatus by a larger metallic vessel of the same form as the smaller one, and of such a size that a certain space is left between them, which is to be filled with pounded ice or snow. No external heat can now penetrate to the inner vessel; because all the caloric derived from the apartment is absorbed by the outer one, and is employed, not in elevating its temperature, but in dissolving the pounded ice within it.

Notwithstanding this precaution, however, the accuracy of the calorimeter may fairly be questioned. That the results obtained by it should be correct, it is essential that all the water which is produced should flow out and be collected. But there is reason to suspect that some of the water is apt to freeze again before it has had time to escape; and if this be true, as *a priori* is very probable, then the information given by the calorimeter must be rejected as useless.

The specific caloric of the gases may be determined in the same way as that of liquids and solids; but as the quantity of heat given out by them in cooling, even through a considerable number of degrees, is very small*, the investigation is one of considerable difficulty. The following table contains the conclusions of Dr Crawford and of Delaroche and Bérard†. Equal weights of each substance are compared together, and the capacities are referred to water as unity.

| | *Delaroche and Bérard.* | *Crawford.* |
|---|---|---|
| Water | 1.0000 | 1.0000 |
| Air | 0.2669 | 1.7900 |
| Hydrogen gas | 3.2936 | 21.4000 |

* This remark of Dr Turner may possibly lead the student into error, and therefore requires some elucidation. It cannot be intended to convey the idea that the specific caloric of gases is *very small*, when compared, in equal weights, with solids; though this is the fact when they are compared in equal volumes with the latter. But in point of fact, as the gases are more easily experimented upon, when taken in a convenient quantity in volume, the weight of which is necessarily small, it follows that, in the investigation of the specific caloric of gases, the quantity of heat to be estimated in any one experiment is proportionably minute. With respect to hydrogen, in no point of view can its specific caloric be considered small; for it is more than three times as great as that of an equal weight of water, taking the results of Delaroche and Bérard. B.

† Annales de Chimie for 1813, or Annals of Philosophy, vol. ii.

| | *Delaroche and Bérard.* | *Crawford.* |
|---|---|---|
| Carbonic acid gas | 0.2210 | 1.0454 |
| Oxygen gas | 0.2361 | 4.7490 |
| Nitrogen gas | 0.2754 | 0.7936 |
| Nitrous oxide gas | 0.2369 | |
| Olefiant gas | 0.4207 | |
| Carbonic oxide gas | 0.2884 | |
| Aqueous vapour | 0.8470 | 1.5500* |

The discordance in these results is a sufficient proof of the difficulty of the inquiry. Dr Crawford had determined by experiment, that solid bodies have a less capacity for caloric than liquids; and it follows, from the numbers contained in the preceding table, that gases in general are superior in this respect to liquids. It had also been observed that the specific caloric of a gas increases when it is dilated, and diminishes when it suffers condensation. It seemed probable from this, that the capacity of the same body for caloric would increase when its density became less, or its cohesion diminished, as when a solid liquefies, or a liquid is converted into vapour. These views were favoured by the experiments of Crawford, but completely overturned by those of Delaroche and Bérard; since, according to the first authority, the specific caloric of watery vapour is much greater than that of water, while, according to the second, it is considerably less.

In drawing a parallel between the two sets of experiments, the preference must certainly be given to those of Delaroche and Bérard. From being the most recent experimenters on the subject, they had all the experience of their predecessors to guide them; and their apparatus, though complicated and difficult to manage, was better suited to the object than that of Crawford. Their results agree, also, with those published in 1819 by MM. Clement and Desormes in the *Journal de Physique* lxxxix. 320; and Mr. Dalton, in the second volume of his Chemical Philosophy, page 282, states that he has repeated the experiment of Delaroche and Bérard on the specific caloric of atmospheric air, and is convinced that their number is very near the truth. The results of Dr Crawford, therefore, must be given up as unworthy of confidence.

But these remarks apply only to the gases. The specific caloric of watery vapour cannot be regarded as known with the same degree of certainty: nor do Delaroche and Bérard themselves place much reliance on the accuracy of their result. This point then must be left to

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* In the above numbers for specific caloric, the several gases are compared in equal weights. According to some recent experiments of Hagenraft, and particularly of Aug. Delarive and Fr. Marcet, it appears that equal volumes of all gases, at the same temperature, and under the same pressure, have the same specific heat. *Berzelius, Traité de Chimie*, i. 89.

It does not appear to be equally true that the same volume of any gas, estimated under different pressures, has the same specific heat. For by the experiments of Delarive and Marcet, the specific caloric is less for the same volume of gas, the less the pressure to which it is subjected. This result corresponds with the observations of Delaroche and Bérard, who found that the specific caloric of a given weight of gas expanded to double its volume, is not doubled, though considerably increased. See note of the author, at page 48. B.

be decided by future observation; for the data which we at present possess cannot be trusted.

The facts hitherto determined concerning the specific caloric of bodies may be arranged under the four following heads.

1. Every substance has a specific caloric peculiar to itself; whence it follows that a change of composition will be attended by a change of capacity for caloric.

2. The specific caloric of a body varies with its form. A solid has a less capacity for caloric than when it is liquid; thus the capacity of water in the solid state is 900, and in the liquid 1000. It was formerly supposed that the same substance has a greater specific caloric in the form of gas than when it is in a solid or liquid form; but the discrepancy above alluded to respecting the comparative specific caloric of water and watery vapour, throws a doubt on this supposition which can be cleared away only by future and more accurate experiments.

3. The specific caloric of all gases increases as their density diminishes, and conversely, the former decreases with the increase of density*. This being the case with elastic fluids, it may reasonably be asked whether the same law does not extend to liquids and solids; whether water, for instance, at 32°, possesses the same specific caloric as when dilated by a high temperature. Drs Crawford and Irvine contended that it is permanent or nearly so, affirming that solids and liquids possess the same specific caloric at all temperatures, so long as they suffer no change of form or composition. Mr Dalton, on the contrary, (Chemical Philosophy, part I. p. 50), in endeavours to show that the specific caloric of such bodies is greater high than in low temperatures; and Petit and Dulong, in the essay already quoted, have proved it experimentally with respect to several of them. Thus the mean capacity of iron between

| | | | | |
|---|---|---|---|---|
| 0° C | and | 100° Cent | is | 0.1098 |
| 0° C | . | 200° C | . | 0.1150 |
| 0° C | . | 300° C | . | 0.1218 |
| 0° C | . | 350° C | . | 0.1255 |

and the same is true of the substances contained in the following Table.

| | | *Mean capacity between* 0° *and* 100° C | | *Mean capacity between* 0° *and* 300° C |
|---|---|---|---|---|
| Mercury | . | 0.0330 | . | 0.0350 |
| Zinc | . | 0.0927 | . | 0.1015 |
| Antimony | . | 0.0507 | . | 0.0549 |
| Silver | . | 0.0557 | . | 0.0611 |
| Copper | . | 0.0949 | . | 0.1013 |
| Platinum | . | 0.0335 | . | 0.0355 |
| Glass | . | 0.1770 | . | 0.1900 |

It is difficult to determine whether the increased specific caloric observed in solids and liquids at high temperatures is owing to the accumulation of heat within them, or to the dilatation. It is ascribed in general to the latter, and I believe correctly; because the expansion and contraction of gases by change of pressure, without the aid of

* Delaroche and Bérard ascertained that the capacity of gases for caloric does not increase in the same ratio as the diminution of density, but according to a less rapid progression. Thus, the specific caloric of any gas being 1, it is not 2 when its bulk is doubled, but between one and two.

heat, is attended with corresponding changes or capacity for caloric.

4. A change of capacity for caloric always occasions a change of temperature. An increase in the former is attended by a diminution of the latter; and a decrease in the former, by an increase of the latter. Thus when air, confined within a flaccid bladder, is suddenly dilated by means of the air-pump, a thermometer placed in it will indicate the production of cold. On the contrary, when air is compressed, the corresponding diminution of its specific caloric gives rise to an increase of temperature; nay, so much heat is evolved when the compression is sudden and forcible, that tinder may be kindled by it. The explanation of these facts is obvious. In the first case, a quantity of caloric becomes insensible, which was previously in a sensible state; in the second, caloric is evolved, which was previously latent.

From some experiments, the result of which is given in the 10th volume of the *An. de Ch. et Ph.*, MM. Dulong and Petit have inferred that the atoms of simple substances have the same capacity for caloric. The following table is taken from their essay. (Page 403.)

| | *Specific Caloric.* | *Relative weights of Atoms.* | *Products of the weight of each Atom by the corresponding capacity.* |
|---|---|---|---|
| Bismuth | 0.0288 | 13.30 | 0.3830 |
| Lead | 0.0293 | 12.95 | 0.3794 |
| Gold | 0.0298 | 12.43 | 0.3704 |
| Platinum | 0.0335 | 11.16 | 0.3740 |
| Tin | 0.0514 | 7.35 | 0.3779 |
| Silver | 0.0557 | 6.75 | 0 3759 |
| Zinc | 0.0927 | 4.03 | 0.3736 |
| Tellurium | 0.0912 | 4.03 | 0.3675 |
| Copper | 0.0949 | 3.957 | 0.3756 |
| Nickel | 0.1035 | 3.69 | 0.3819 |
| Iron | 0.1100 | 3.392 | 0.3731 |
| Cobalt | 0.1498 | 2.46 | 0.3685 |
| Sulphur | 0.1880 | 2.011 | 0.3780* |

In the new part of his Chemical Philosophy, page 293, Mr Dalton has made some strictures in reference to this table, tending to show that the opinion of Dulong and Petit cannot be correct, and stands in opposition to their own facts. Mr Dalton argues that the product of the weight of an atom by the corresponding capacity for caloric, is not a constant quantity; because the capacity of the same substance varies with change of form, or even, according to their own experiments, from variation of temperature without change of form. To the latter part of the criticism, Dulong and Petit are certainly exposed; but they have anticipated the former by remarking, that the law is not affected by change of form, provided the substances compared are taken in the same state. Whether this position is or is not correct, remains to be proved.

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* If the atomic weights contained in this table were corrected according to the latest determinations, the coincidences between the specific heats of the atoms would be far less striking. See some interesting strictures on this table by Professor A. D. Bache, of the University of Pennsylvania, contained in the Journal of the Academy of Natural Sciences of Philadelphia, for January 1829. B.

## On Liquefaction.

All bodies. hitherto known, are either solid, liquid, or gaseous; and the form they assume depends on the relative intensity of cohesion and repulsion. Should the repulsive force be comparatively feeble, the particles will adhere so firmly together that they cannot move freely upon one another, thus constituting a solid. If cohesion is so far counteracted by repulsion, that the particles move on each other freely, a liquid is formed. And should the cohesive attraction be entirely overcome, so that the particles not only move freely on each other, but separate from one another to an almost indefinite extent unless restrained by external pressure, an aeriform substance will be produced.

Now the property of repulsion is manifestly owing to caloric; and as it is easy within certain limits to increase or diminish the quantity of this principle in any substance, it follows that the form of bodies may be made to vary at pleasure; that is, by a sufficiently intense heat, every solid may be converted into a fluid, and every fluid into the aeriform state. This inference is justified by experience so far, that it may safely be considered a general law. The converse ought also to be true; and, accordingly, several of the gases have already been condensed by means of pressure into liquids, and liquids have been solidified by cold. The temperature at which liquefaction takes place is called the melting point, or point of fusion; and that at which liquids solidify, their point of congelation. Both these points are different for different substances, but uniformly the same, under similar circumstances, in the same body.

The most important circumstance relative to liquefaction is the discovery of Dr Black, that a large quantity of caloric disappears, or becomes insensible to the thermometer, during the process. If a pound of water at 32° be mixed with a pound of water at 172°, the temperature of the mixture will be intermediate between them, or 102°. But if a pound of water at 172° be added to a pound of ice at 32°, the ice will quickly dissolve, and on placing a thermometer in the mixture, it will be found to stand, not at 102°, but at 32°. In this experiment, the pound of hot water, which was originally at 172°, actually loses 140 degrees of caloric, all of which entered into the ice, and caused its liquefaction, but did not affect its temperature; and it follows, therefore, that a quantity of caloric becomes insensible during the melting of ice, sufficient to raise the temperature of an equal weight of water 140 degrees of Fahrenheit. This explains the well known fact, on which the graduation of the thermometer depends,—that the temperature of melting ice or snow never exceeds 32° F. All the caloric which is added becomes insensible, till the liquefaction is complete.

The loss of sensible caloric which attends liquefaction seems essentially necessary to the change, and for that reason is frequently called the *caloric of fluidity*. The actual quantity of caloric required for this purpose varies with the substance, as is proved by the following results obtained by Irvine. The degrees indicate the extent to which an equal weight of each material may be heated by the caloric of fluidity which is proper to it.

| | *Caloric of Fluidity.* |
|---|---|
| Sulphur | 143.68° F. |
| Spermaceti | 145° |
| Lead | 162° |
| Bees-wax | 175° |
| Zinc | 493° |
| Tin | 500° |
| Bismuth | 550° |

As so much heat disappears during liquefaction, it follows that caloric must be evolved when a liquid passes into a solid. This may easily be proved. The temperature of water in the act of freezing never falls below 32° F. though it be exposed to an atmosphere in which the thermometer is at zero. It is obvious that the water can preserve its temperature in a medium so much colder than itself, only by the caloric which it loses being instantly supplied; and it is no less clear that the only source of supply is the caloric of fluidity. Further, if pure recently boiled water be cooled very slowly, and kept very tranquil, its temperature may be lowered to 21° F. without any ice being formed; but the least motion causes it to congeal suddenly, and in doing so, its temperature rises to 32° F.*

The explanation which Dr Black gave of these phenomena constitutes what is called his *Doctrine* of *latent heat*, which was partially explained on a former occasion. (Page 44.) He conceived that caloric in causing fluidity loses its property of acting on the thermometer in consequence of combining chemically with the solid substance, and that liquefaction results, because the compound so formed does not possess that degree of cohesive attraction on which solidity depends. When a liquid is cooled to a certain point, it parts with its caloric of fluidity, heat is set free or becomes sensible, and the cohesion natural to the solid is restored. The same mode of reasoning was applied by Dr Black to the conversion of liquids into vapours, during which change a large quantity of caloric disappears.

A different explanation of these phenomena was proposed by Dr Irvine. Observing that a solid has a less capacity for caloric than the same substance when in a liquid state, he argued that this circumstance alone accounts for caloric becoming insensible during liquefaction. For since the capacity of ice and water for caloric, or in other words the quantity of heat required to raise their temperature by the same number of degrees, was found to be as 9 to 10, Dr Irvine inferred that water must contain one-ninth more caloric than ice of the same temperature, and that as this difference must be supplied to the ice when it is converted into water, this change must necessarily be accompanied with the disappearance of caloric. Dr Irvine applied the same argument to the liquefaction of all solids, and likewise to account for the caloric which is rendered insensible during the formation of vapour.

Two objections may properly be urged against the opinion of Dr Irvine. In the first place, no adequate reason is assigned for the liquefaction. It accounts for the disappearance of caloric which accompanies liquefaction, but does not explain why the body becomes liquid; whereas the hypothesis of Dr Black affords an explanation both of the change itself, and of the phenomena that attend it. But the second objection is still more conclusive. Dr Irvine argued on the belief that a liquid has in every case a greater capacity for caloric than when in the solid state; and though this point has not been demonstrated in a manner entirely decisive, yet from the experiments hitherto made it appears that liquids in general have a greater specific caloric than solids, and that therefore Dr Irvine's assumption is probably correct. In like manner he believed vapours to have a greater capacity for caloric than the liquids that yield them, and his opinion was supported by the experiments of Crawford on the specific caloric of water and watery vapour. But no reliance whatever can be placed in

* Sir Ch. Blagden, in Philos. Trans. for 1788.

the researches of Dr Crawford on this subject; not only because his result is so different from that obtained by Delaroche and Bérard, but because all his other experiments on the specific caloric of elastic fluids are decidedly erroneous. (Page 46.) Indeed from the fact of most gases having a less specific caloric than liquids, it is probable that the capacity of elastic fluids in general for caloric is inferior to that of the liquids from which they are derived*. The disappearance of caloric during vaporization is therefore not explicable on the views of Irvine; it is necessary to employ the theory of Dr Black to account for that change, and therefore the same doctrine should be applied to the analogous phenomenon of liquefaction.

In speculating on the cause of the specific caloric of bodies at page 44, I had recourse to the doctrine of latent or combined caloric. Dr Black restricted the use of this hypothesis to explain the phenomena of liquefaction and vaporization; but I apprehend it may be applied without impropriety to all cases where caloric passes from a sensible to an insensible state. That this may happen when caloric enters a body, without change of form, is easily demonstrated. Thus, in order to raise an equal weight of water and mercury by the same number of degrees, it is necessary to add 28 times as much heat to the water as to the mercury; a fact which proves that a quantity of caloric becomes insensible to the thermometer when the temperature of water is raised by one degree, just as happens when ice is converted into water, or water into vapour†. The phenomena are in this point of view identical; and, therefore, the same mode of reasoning by which one of them is explained, may be employed to account for the other.

The disappearance of sensible caloric in liquefaction is the basis of many artificial processes for producing cold. All of them are conducted on the principle of liquefying solid substances without the aid of heat. For the caloric of fluidity being then derived chiefly from that which had previously existed within the solid itself in a sensible state, the temperature necessarily falls. The degree of cold thus produced depends upon the quantity of caloric which disappears, and this again is dependent on the quantity of solid liquefied, and the rapidity of liquefaction.

The most common method of producing cold is by mixing together equal parts of snow and salt. The salt causes the snow to melt by reason of its affinity for water, and the water dissolves the salt, so that both of them become liquid. The cold thus generated is 32 degrees below the temperature of freezing water; that is, a thermometer placed in the mixture would stand at zero. This is the way originally proposed by Fahrenheit for determining the commencement of his scale.

Any other substances which have a strong affinity for water may be substituted for the salt; and those have the greatest effect in producing cold whose affinity for that liquid is greatest, and which consequently produce the most rapid liquefaction. The crystallized muriate of lime, proposed by Lowitz, is by far the most convenient in practice. This salt may be made by dissolving marble in muriatic acid. The solution should be concentrated by evaporation, till upon letting a drop of it fall upon a cold saucer, it becomes a solid mass. It should then be withdrawn from the fire, and when cold be speedily reduced to a fine powder. From its extreme deliquescence it must

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* See note, page 46, relating to this point. B.

† See note, p. 44, where this view of the subject is controverted. B.

be preserved in well-stopped vessels. The following table, from Mr Walker's paper in the Philosophical Transactions for 1801, contains the best proportions for producing intense cold.

## *Frigorific Mixtures with Snow*.*

| MIXTURES. | Parts by Weight. | *Thermometer sinks* | *Degree of Cold produced.* |
|---|---|---|---|
| Muriate of Soda | 1 | From any temperature to — 5° | |
| Snow | 2 | | |
| Muriate of Soda | 2 | to — 12° | |
| Muriate of Ammonia | 1 | | |
| Snow | 5 | | |
| Muriate of Soda | 10 | to — 18° | |
| Muriate of Ammonia | 5 | | |
| Nitrate of Potassa | 5 | | |
| Snow | 24 | | |
| Muriate of Soda | 5 | to — 25° | |
| Nitrate of Ammonia | 5 | | |
| Snow | 12 | | |
| †Diluted Sulphuric Acid | 2 | from + 32° to + 23° | 55 degrees. |
| Snow | 3 | | |
| Concentrated Muriatic Acid | 5 | from + 32° to — 27° | 59 |
| Snow | 8 | | |
| Concentrated Nitrous Acid | 4 | from + 32° to — 30° | 62 |
| Snow | 7 | | |
| Muriate of Lime | 5 | from + 32° to — 40° | 72 |
| Snow | 4 | | |
| Crystallized Muriate of Lime | 3 | from + 32° to — 50° | 82 |
| Snow | 2 | | |
| Fused Potassa | 4 | from + 32° to — 51° | 83 |
| Snow | 3 | | |

But freezing mixtures may be made by the rapid solution of salts, without the use of snow or ice; and the following table, taken from Walker's paper in the Philos. Trans. for 1795, includes the most important of them. The salts must be finely powdered and dry.

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* The snow should be freshly fallen, dry and uncompressed. If snow cannot be had, finely pounded ice may be substituted for it.

† Made of strong acid, diluted with half its weight of snow or distilled water.

| MIXTURES. Parts by Weight. | | *Temperature falls* | *Degree of Cold produced.* |
|---|---|---|---|
| Muriate of Ammonia<br>Nitrate of Potassa<br>Water | 5<br>5<br>16 | from + 50° to + 10° | 40 degrees. |
| Muriate of Ammonia<br>Nitrate of Potassa<br>Sulphate of Soda<br>Water | 5<br>5<br>8<br>16 | from + 50° to + 4° | 46 |
| Nitrate of Ammonia<br>Water | 1<br>1 | from + 50° to + 4° | 46 |
| Nitrate of Ammonia<br>Carbonate of Soda<br>Water | 1<br>1<br>1 | from + 50° to — 7° | 57 |
| Sulphate of Soda<br>Diluted Nitrous Acid* | 3<br>2 | from + 50° to — 3° | 53 |
| Sulphate of Soda<br>Muriate of Ammonia<br>Nitrate of Potassa<br>Diluted Nitrous Acid | 6<br>4<br>2<br>4 | from + 50° to — 10° | 60 |
| Sulphate of Soda<br>Nitrate of Ammonia<br>Diluted Nitrous Acid | 6<br>5<br>4 | from + 50° to — 14° | 64 |
| Phosphate of Soda<br>Diluted Nitrous Acid | 9<br>4 | from + 50° to — 12° | 62 |
| Phosphate of Soda<br>Nitrate of Ammonia<br>Diluted Nitrous Acid | 9<br>6<br>4 | from + 50° to — 21° | 71 |
| Sulphate of Soda<br>Muriatic Acid | 8<br>5 | from + 50° to 0° | 50 |
| Sulphate of Soda<br>Diluted Sulphuric Acid† | 5<br>4 | from + 50° to + 3° | 47 |

These artificial processes for generating cold are much more effectual when the materials are previously cooled by immersion in other frigorific mixtures. One would at first suppose that an unlimited degree of cold may be thus produced; but it is found that when the difference between the mixture and the air becomes very great, caloric is so rapidly communicated from one to the other, as to limit the reduction to a certain point. The greatest cold produced by Mr Walker, did not exceed 100 degrees below the zero of Fahrenheit.

Though it is unlikely that we shall ever succeed in depriving any substance of all its caloric, it is presumed that bodies do contain a certain definite quantity of this principle, and various attempts have been made to calculate its amount. The mode of conducting such a calculation may be shown by the process of Dr Irvine. That ingenious chemist proceeded on the assumption, that the actual quantity of caloric in bodies is proportioned to their capacity, and that the capacity

* Composed of fuming nitrous acid two parts in weight and one of water, the mixture being allowed to cool before being used.

† Composed of equal weights of strong acid and water, being allowed to cool before use.

remains the same at all temperatures, provided no change of form takes place. Thus, as the capacity of ice is to that of water as 9 to 10, it follows, according to the hypothesis, that water at 32° must lose 1-10th of its caloric to be converted into ice*. Now Dr Black ascertained that this tenth, which is the caloric of fluidity, is equal to 140 degrees; whence it was inferred that water at 32° contains 10 times 140 or 1400 degrees of caloric.

To be satisfied that such calculations cannot be trusted, it is sufficient to know, that the estimates made by different chemists respecting the absolute quantity of caloric in water vary from 900 to nearly 8000†. Besides, even did the estimates agree with one another, the principle of the calculation would still be unsatisfactory; for, in the first place, there is no proof that the quantity of heat in bodies is in the ratio of their capacities; and, secondly, the assumption that the capacity of a body for caloric is the same at all temperatures, so long as it does not experience a change of form, has been proved to be erroneous by the experiments of Dulong and Petit.

## *Vaporization.*

Aeriform substances are commonly divided into vapours and gases. The character of the former is, that they may be readily converted into liquids or solids, either by a moderate increase of pressure, the temperature at which they were formed remaining the same, or by a moderate diminution of that temperature, without change of pressure. Gases, on the contrary, retain their elastic state more obstinately; they are always gaseous at common temperatures, and, with one or two exceptions, cannot be made to change their form, unless by being subjected to much greater pressure than they are naturally exposed to. Several of them, indeed, have hitherto resisted every effort to compress them into liquids. The only difference between gases and vapours is in the relative forces with which they resist condensation.

Caloric appears to be the cause of vaporization, as well as of liquefaction, and it is a general opinion that a sufficiently intense heat would convert every liquid and solid into vapour. A considerable number of bodies, however, resist the strongest heat of our furnaces without vaporizing. These are said to be *fixed* in the fire; those which, under the same circumstances, are converted into vapour, are called *volatile*.

The disposition of various substances to yield vapour is very different; and the difference depends doubtless on the relative power of cohesion with which they are endowed. Fluids are, in general, more easily vaporized than solids, as would be expected from the weaker cohesion of the former. Some solids, such as arsenic and sal-ammoniac, pass at once into vapour without being liquefied; but most of them become liquid before assuming the elastic condition.

Vapours occupy more space than the substances from which they were produced. According to the experiments of Gay-Lussac, water,

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* A slight inaccuracy existed in the author's text in this place, which I have taken the liberty to correct. It is evident that 10 is not 1-10th more than 9. Another inaccuracy relating to the same subject was corrected in the account of Dr Irvine's views (page 51) where in the original it was stated that water contained "*ten times* more caloric than ice of the same temperature." B.

† Dalton's New System of Chemical Philosophy.

at its point of greatest density, in passing into vapour, expands to 1696 times its volume, alcohol to 659 times, and ether to 443 times, each vapour being at a temperature of 212° F. and under a pressure of 29·92 inches of mercury. This shows that vapours differ in density. Watery vapour is lighter than air at the same temperature and pressure, in the proportion of 1000 to 1604; or the density of air being 1000, that of watery vapour is 623. The vapour of alcohol, on the contrary, is half as heavy again as air; and that of ether is more than twice and a half as heavy. As alcohol boils at a lower temperature than water, and ether than alcohol, it was conceived that the density of vapours might be in the direct ratio of the volatility of the liquids which produced them. But Gay-Lussac has shown that this law does not hold generally; for the carburet of sulphur boils at a higher temperature than ether, and nevertheless it yields the heavier vapour.

The dilatation of vapours by heat was found by Gay-Lussac to follow the same law as gases, that is, for every degree of Fahrenheit, they increase by 1-480th of the volume they occupied at 32°. But the law does not hold unless the quantity of vapour continues the same. If the increase of temperature cause a fresh portion of vapour to rise, then the expansion will be greater than 1-480th, for each degree; because the heat not only dilates the vapour previously existing to the same extent as if it were a real gas, but augments its bulk by adding a fresh quantity of vapour. The contraction of a vapour on cooling will likewise deviate from the above law, whenever the cold converts any of it into a liquid—an effect which must happen, if the space had originally contained its maximum of vapour. Thus aqueous vapour at 32° supports a column of only 0·2 of an inch, while at 212° its elasticity is equal to a pressure of 30 inches of mercury. Hence the elastic force or expansion of watery vapour between 32° and 212°, supposing the space to be in a state of saturation, is as 1 to 150.

Vaporization is conveniently studied under two heads,—*Ebullition* and *Evaporation*. In the first, the production of vapour is so rapid that its escape gives rise to a visible commotion in the liquid: in the second, it passes off quietly and insensibly.

## *Ebullition.*

The temperature at which vapour rises with sufficient freedom for causing the phenomena of ebullition, is called the *boiling point*. The heat requisite for this effect varies with the nature of the fluid. Thus, sulphuric ether boils at 96° F. alcohol at 173°, and pure water at 212°; while oil of turpentine must be raised to 316°, and mercury to 680° before either exhibits marks of ebullition. The boiling point of the same liquid is constant, so long as the necessary conditions are preserved; but it is liable to be affected by several circumstances. The nature of the vessel has some influence upon it. Thus, Gay-Lussac observed that pure water boils precisely at 212° in a metallic vessel, and at 214° in one of glass. It is likewise affected by the presence of foreign particles. The same accurate experimenter found, that when a few iron filings are thrown into water boiling in a glass vessel, its temperature quickly falls from 214° to 212°, and remains stationary at the last point. But the circumstance which has the greatest influence over the boiling point of fluids is variation of pressure. All bodies upon the earth are constantly exposed to considerable pressure; for the atmosphere itself presses with a force equivalent to a weight of 15 pounds on every square inch of surface.

Liquids are exposed to this pressure as well as solids, and their tendency to take the form of vapour is very much counteracted by it. In fact they cannot enter into ebullition at all, till their particles have acquired such an elastic force as enables them to overcome the pressure upon their surfaces; that is, till they press against the atmosphere with the same force as the atmosphere against them. Now the atmospheric pressure is variable, and hence it follows that the boiling point of liquids must also vary.

The only time at which the pressure of the atmosphere is equal to a weight of 15 pounds on every square inch of surface, is when the barometer stands at 30 inches, and then only does water boil at 212° F. If the pressure be less, that is, if the barometer fall below 30 inches, then the boiling point of water, and every other liquid will be lower than usual; or if the barometer rises above 30 inches, the temperature of ebullition will be proportionally increased. This is the reason why water boils at a lower temperature on the top of a hill than in the valley beneath it; for as the column of air diminishes in length as we ascend, its pressure must likewise suffer a proportional diminution. The ratio between the depression of the boiling point and the diminution of the atmospherical pressure is so exact, that it has been proposed as a method for determining the heights of mountains*. An elevation of 530 feet makes a diminution of one degree of Fahrenheit.

The influence of the atmosphere over the point of ebullition is best shown by removing its pressure altogether. The late Professor Robinson found that fluids boil in vacuo at a temperature 140 degrees lower than in the open air†. Thus water boils in vacuo at 72°, alcohol at 33°, and ether at —44° F. This proves that a liquid is not necessarily hot, because it boils. The heat of the hand is sufficient to make water boil in vacuo, as is exemplified by the common pulse-glass; and ether, under the same circumstances, will enter into ebullition, though its temperature is low enough for freezing mercury.

Water cannot be heated under common circumstances beyond 212°, because it then acquires such an expansive force as enables it to overcome the atmospheric pressure, and fly off in the form of vapour. But if subjected to sufficient pressure, it may be heated to any extent without boiling. This is best done by heating water while confined in a strong copper vessel, called Papin's Digester. In this apparatus, on the application of heat, a large quantity of vapour collects above the water, which checks the ebullition by the pressure it exerts upon the surface of the liquid. There is no limit to which water may be heated in this way, provided the vessel is strong enough to confine the vapour; but the expansive force of steam under these circumstances is so enormous as to overcome the greatest resistance.

In estimating the power of steam, it should be remembered that vapour, if separated from the liquid which produced it, does not possess a greater elasticity than an equal quantity of air. If, for example, the digester was full of steam at 212°, no water in the liquid state being present, it may be heated to any degree, even to redness, without danger of bursting. But if water be present, then each addition of caloric causes a fresh portion of steam to rise, which adds its own elastic force to that of the vapour previously existing; and in conse-

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* Wollaston in Phil. Trans. 1817.
† Black's Lectures, p. 151.

quence an excessive pressure is soon exerted against the inside of the vessel. Professor Robison (Brewster's edition of his works, p. 25) found that the tension of steam is equal to two atmospheres at 244° F. and to three at 270° F. The results of Mr Southern's experiments, given in the same volume, fix upon 250·3° F. as the temperature at which steam has the force of two atmospheres, on 293·4° F. for four, and 343·6° F. for eight atmospheres.

The elasticity of steam is employed as a moving power in the steam-engine. The construction of this machine depends on two properties of steam, namely, the expansive force communicated to it by caloric, and its ready conversion into water by cold. The effect of both these properties is well shown by a little instrument devised by Dr Wollaston. It consists of a cylindrical glass tube, six inches long, nearly an inch wide, and blown out into a spherical enlargement at one end. A piston is accurately fitted to the cylinder, so as to move up and down the tube with freedom. When the piston is at the bottom of the tube, it is forced up by causing a portion of water, previously placed in the ball, to boil by means of a spirit-lamp. On dipping the ball into cold water, the steam which occupies the cylinder is suddenly condensed, and the piston forced down by the pressure of the air above it. By the alternate application of heat and cold, the same movements are reproduced, and may be repeated for any length of time.

The moving power of the steam engine is the same as in this apparatus. The only essential difference between them is in the mode of condensing the steam. In the steam-engine, the steam is condensed in a separate vessel called the *condenser*, where there is a regular supply of cold water for the purpose. By this contrivance, which constitutes the great improvement of Watt, the temperature of the cylinder never falls below 212°.

The formation of vapour is attended, like liquefaction, with a loss of sensible caloric. This is proved by the well-known fact that the temperature of steam is precisely the same as that of boiling water from which it rises; so that all the caloric which enters into the liquid is solely employed in converting a portion of it into vapour, without affecting the temperature of either in the slightest degree, provided the latter is permitted to escape with freedom. The caloric which then becomes latent, to use the language of Dr Black, is again set free when the vapour is condensed into water. The exact quantity of caloric rendered insensible by vaporization, may therefore be ascertained by condensing the vapour in cold water, and observing the rise of temperature occasioned by it. From the experiments of Dr Black and Mr Watt, conducted on this principle, it appears that steam of 212°, in being condensed into water of 212°, gives out as much caloric as would raise the temperature of an equal weight of water by 950 degrees, all of which had previously existed in the vapour without being sensible to a thermometer.

The latent heat of steam and several other vapours has been examined by Dr Ure*, whose results are contained in the following table.

| | *Latent Heat.* |
|---|---|
| Vapour of Water at its boiling point | 967° |
| Alcohol | 442 |
| Ether | 302.379 |
| Petroleum | 177.87 |

* Philos. Trans. 1818.

| | Latent Heat. |
|---|---|
| Vapour of Oil of turpentine . . | 177.87 |
| Nitric acid . . | 531.99 |
| Liquid ammonia . . | 837.28 |
| Vinegar . . | 875 |

The disappearance of caloric that accompanies vaporization was explained by Dr Black and Dr Irvine, in the way already mentioned under the head of liquefaction; and as the objections to the views of the latter ingenious chemist were then stated, it is unnecessary to mention them on the present occasion.

## *Evaporation.*

Evaporation as well as ebullition consists in the formation of vapour, and the only assignable difference between them is, that the one takes place quietly, the other with the appearance of boiling. Evaporation takes place at common temperatures, as may be proved by exposing water in a shallow vessel to the air for a few days, when it will gradually diminish, and at last disappear entirely. Most fluids, if not all of them, are susceptible of this gradual dissipation; and it may also be observed in some solids, as for example in camphor. Evaporation is much more rapid in some fluids than in others, and it is always found that those liquids, whose boiling point is lowest, evaporate with the greatest rapidity. Thus alcohol, which boils at a lower temperature than water, evaporates also more freely; and ether, whose point of ebullition is yet lower than that of alcohol, evaporates with still greater rapidity.

The chief circumstances that influence the process of evaporation are extent of surface, and the state of the air as to temperature, dryness, stillness, and density.

1. Extent of surface. Evaporation proceeds only from the surface of fluids, and therefore, *cæteris paribus*, must depend upon the extent of surface exposed.

2. Temperature. The effect of heat in promoting evaporation may easily be shown by putting an equal quantity of water into two saucers, one of which is placed in a warm, the other in a cold situation. The former will be quite dry before the latter has suffered an appreciable diminution.

3. State of the air as to dryness or moisture. When water is covered by a stratum of dry air, the evaporation is rapid even when its temperature is low. Thus in some dry cold days in winter, the evaporation is exceedingly rapid; whereas it goes on very tardily, if the atmosphere contains much vapour, even though the air be very warm.

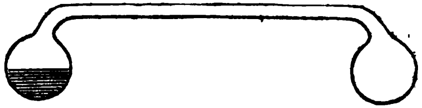
4. Evaporation is far slower in still air than in a current, and for an obvious reason. The air immediately in contact with the water soon becomes moist, and thus a check is put to evaporation. But if the air is removed from the surface of the water as soon as it has become charged with vapour, and its place supplied with fresh dry air, then the evaporation continues without interruption.

5. Pressure over the surface of liquids has a remarkable influence over evaporation. This is easily proved by placing ether in the vacuum of an air pump, when vapour rises so abundantly as to produce ebullition.

As a large quantity of caloric passes from a sensible to an insensible state during the formation of vapour, it follows that cold should be generated by evaporation. A very simple experiment will prove it. If a few drops of ether be allowed to fall upon the hand, a strong sen-

sation of cold will be excited during the evaporation; or if the bulb of a thermometer, covered with lint, be moistened with ether, the production of cold will be marked by the descent of the mercury. But to appreciate the degree of cold which may be produced by evaporation, it is necessary to render it very rapid and abundant by artificial processes; and the best means of doing so, is by removing pressure from the surface of volatile liquids. Water placed under the exhausted receiver of an air-pump, evaporates with great rapidity, and so much cold is generated as would freeze the water, did the vapour continue to rise for some time with the same velocity. But the vapour itself soon fills the vacuum, and retards the evaporation by pressing upon the surface of the water. This difficulty may be avoided by putting under the receiver a substance, such as sulphuric acid, which has the property of absorbing watery vapour, and consequently of removing it as quickly as it is formed. Such is the principle of Mr Leslie's method for freezing water by its own evaporation*.

The action of the cryophorus, an ingenious contrivance of Dr Wollaston, depends on the same principle. It consists of two glass balls, perfectly free from air, and joined together by a tube as here represented.



One of the balls contains a portion of distilled water, while the other parts of the instrument, which appear empty, are full of aqueous vapour, which checks the evaporation from the water by the pressure it exerts upon its surface. But when the empty ball is plunged into a freezing mixture, all the vapour within it is condensed; evaporation commences from the surface of the water in the other ball, and it is frozen in two or three minutes by the cold thus produced.

Liquids which evaporate more rapidly than water, cause a still greater reduction of temperature. The cold produced by the evaporation of ether in the vacuum of the air-pump, is so intense as under favourable circumstances to freeze mercury†.

Scientific men have differed concerning the cause of evaporation. It was once supposed to be owing to a chemical attraction between the air and water, and the idea is at first view plausible, since a certain degree of affinity does to all appearance exist between them. But it is nevertheless impossible to attribute the effect to this cause. For evaporation takes place equally in *vacuo* as in the air; nay, it is an established fact, that the atmosphere positively retards the process, and that one of the best means of accelerating it, is by removing the air altogether. The experiments of Mr Dalton prove that caloric is the true and only cause of the formation of vapour. He finds that the actual quantity of vapour which can exist in any given space, is dependent solely upon the temperature. If, for instance, a little water be put into a dry glass flask, a quantity of vapour will be formed proportional to the temperature. If a thermometer placed in it stands at 32°

* See art. Cold in the Supplement to the Encyclopædia Britannica.

† See a paper by the late Dr Marcet, in Nicholson's Journal, vol. xxxiv.

F. the flask will contain a very small quantity of vapour. At 40°, more vapour will exist in it; at 50° it will contain still more; and at 60°, the quantity will be still further augmented. If, when the thermometer is at 60°, the temperature of the flask is suddenly reduced to 40°, then a certain portion of vapour will be converted into water; the quantity which retains the elastic form being precisely the same as when the temperature was originally at 40°.

It matters not with regard to these changes, whether the flask is full of air, or altogether empty; for in either case, it will eventually contain the same quantity of vapour, when the thermometer is at the same height. The only effect of a difference in this respect, is in the rapidity of evaporation. The flask, if previously empty, acquires its full complement of vapour, or, in common language, becomes saturated with it, in an instant; whereas the presence of air affords a mechanical impediment to its passage from one part of the flask to another, and therefore an appreciable time elapses before the whole space is saturated.

Mr Dalton found that the tension or elasticity of vapour is always the same, however much the pressure may vary, so long as the temperature remains constant, and liquid enough is present for preserving the state of saturation proper to the temperature. If, for example, in a vessel containing a liquid, the space occupied by its vapour should suddenly dilate, the vapour it contains will dilate also, and consequently suffer a diminution of elastic force; but its tension will be quickly restored, because the liquid yields an additional quantity of vapour, proportional to the increase of space. Again, if the space be diminished, the temperature remaining constant, the tension of the confined vapour will still continue unchanged; because a quantity of it will be condensed proportional to the diminution of space, so that, in fact, the remaining space contains the very same quantity of vapour as it did originally. The same law holds good whether the vapour is pure or mixed with air or any other gas.

The elasticity of watery vapour at temperatures below 212° F. was carefully examined by Mr Dalton; (Manchester Memoirs, vol. v.) and his results, together with those since obtained by Dr Ure*, are presented in a tabular form at the end of the volume. They were obtained by introducing a portion of water into the vacuum of a common barometer, and estimating the tension of its vapour by the extent to which it depressed the column of mercury at different temperatures. But Mr Dalton did not confine his researches to water; he extended them to the vapour of various liquids, such as ether, alcohol, ammonia, and solution of muriate of lime, and inferred from them the following law:—That the force of vapour from all liquids is the same, at equal distances above or below the several temperatures at which they boil in the open air. Thus steam at 200° F. has the same elasticity as the vapour of ether at 85°, the boiling point of the former being 212°, and of the latter 97°. Biot and Amédé Berthollet (Biot, Traité de Ph. i. 282,) have found that this law applies exactly to many other liquids; but some experiments by Dr Ure on the oil of turpentine and petroleum, would lead to the conclusion that it is not universal.

It is easy, on this principle, to account for the elastic force of the vapours of liquids, whose boiling point is very high, being inappreciable at moderate temperatures. Thus sulphuric acid boils at 620° F.

* Philos. Trans. 1818.

and therefore at 212°, that is 408 degrees below its point of ebullition, the elasticity of its vapour should be equal to that of aqueous vapour at — 196°, or 408 degrees below the boiling point of water. In like manner mercury, which boils at 680°, yields vapour whose elastic force at 212° may be estimated as equal to that of watery vapour at — 256°, or 468 degrees below the point at which water enters into ebullition. According to the same law, mercury requires a temperature of 500°, or 180 degrees below its boiling point, in order that its vapour should have the same tension as watery vapour at 32°. From these considerations it is inferred, that, though in a common barometer the space above the column may contain a little mercurial vapour, and consequently may not be an absolute vacuum, the influence of that vapour in depressing the column, even at considerable temperatures, is altogether inappreciable.

It admits of inquiry whether liquids of weak volatility, such as mercury and oil of vitriol, give off any vapour at common temperatures. An opinion has prevailed, that evaporation not only takes place from the surface of these and similar liquids at all times, but that vapour of exceedingly weak tension is emitted at common temperatures from all substances however fixed in the fire, even from the earths and metals, when they are either placed in a vacuum, or surrounded by gaseous matter. It has accordingly been supposed, that the atmosphere contains diffused through it minute quantities of the vapours of all the bodies with which it is in contact; and this idea has been made the basis of a theory of the origin of meteorites. But this doctrine has been successfully combated by Mr Faraday in his essay On the Existence of a Limit to Vaporization, published in the Philosophical Transactions for 1826. The argument employed by Mr Faraday is founded on the principle, by which Dr Wollaston has accounted for the limited extent of the atmosphere. Since the volume of gaseous substances is dependent on the pressure to which they are subject, the air in the higher regions of the atmosphere must be much more rare than that in the lower, because the former sustains the pressure of a shorter atmospheric column than the latter; so that in ascending upwards from the earth, each successive stratum of air, being less compressed than the foregoing, is likewise more attenuated. Now it is found experimentally that the elasticity or tension of any gaseous matter diminishes in the same ratio as its volume increases; and, accordingly, whenever the tenuity of a portion of air, owing to its distance from the earth's surface or any other cause, is exceedingly great, its tension is exceedingly small. Reasoning on this principle, Dr Wollaston conceives that at a certain altitude, probably at a distance of 40 or 50 miles from the surface of the earth, the rarefaction and consequent loss of elastic force is so extreme, that the mere gravity of the particles becomes equal to their elasticity, and thus puts a limit to their separation.

What Dr Wollaston suggests of aerial particles, Mr Faraday supposes to occur in all substances; and this supposition is perfectly legitimate, because gaseous matter in general is subject to the same law of expansion, and is likewise under the influence of gravity. He infers that every kind of matter ceases to assume the elastic form whenever the gravitation of its particles is stronger than the elasticity of its vapour. The loss of tension necessary for effecting this object may be accomplished in two ways, either by extreme dilatation, or by cold. For substances of great volatility, such as air and most gases, the former is necessary; because the degree of cold which we can command at the earth's surface diminishes their tension in a degree quite

insufficient for the purpose. But the volatility of innumerable bodies is so small, that their vapour at common temperatures approximates in rarity to the air at the limits of the atmosphere, and a small degree of cold may suffice for rendering its elasticity a force inferior to its opponent, gravity. In that case, the vapour would be entirely condensed. Mr Faraday found that mercury, at a temperature varying from 60° to 80° yields a small quantity of vapour, but in winter no trace of vapour could be detected. Hence it is inferred, that at the former temperature the elasticity of mercurial vapour is slightly superior to the gravity of its particles, and that in cold weather the latter power preponderates, and puts an entire check to the evaporation of mercury. The earths and metals, which are more fixed than mercury, have vapours of such feeble tension, that the highest natural temperature is unable to convert them into vapour. Another force which co-operates with gravity in overcoming elasticity is the attraction of aggregation, or the attraction exerted by a solid or liquid to the contiguous particles of the same substance in the gaseous form. This argument affords very sufficient grounds for believing that the vapours of earthy and metallic substances are never present in the atmosphere.

The presence of vapour has a considerable influence over the bulk of gases; and as chemists often find it convenient to determine the quantity of gaseous substances by measure, it is important to estimate the effect thus produced, in order to make allowance for it. The mode by which a vapour acts is obvious. If a few drops of water are added to a portion of dry air, confined in a glass tube over mercury, the air will speedily become saturated with vapour, and must in consequence be increased in bulk. For the elastic power of the vapour being added to that previously exerted by the gas alone, the mixture will necessarily exert a stronger pressure upon the mercury that confines it, and will therefore occupy a greater space. It is equally clear that the degree of augmentation will depend on the temperature; for it is the temperature alone which determines the tension of the vapour.

As the elastity of vapour is not at all affected by mere admixture with gases, it is easy to correct the fallacy to which its presence gives rise by means of the data furnished by the experiments of Dalton. The formula for the correction is thus deduced*. Let $n$ be the bulk of dry air or other gas expressed in the degrees of a graduated tube; $p$ the tension of the dry air, equal to the atmospheric pressure; $n'$ the bulk of the air when saturated with watery vapour, and $f$ the tension of that vapour.

It is a well-known law in pneumatics that the elasticity of a gas is inversely as its volume; so that, when the dry air increases in bulk from $n$ to $n'$, its elasticity diminishes in the ratio of $n'$ to $n$. Hence its elasticity ceases to be $= p$, but is expressed by $\frac{pn}{n'}$; $p$ is now $= \frac{pn}{n'} + f$; that is, the elasticity of the dilated air, added to the elasticity of the vapour present, is equal to the pressure of the atmosphere. From this last equation are deduced the following values: $pn + fn' = pn'$; $pn = pn' - fn'$; and $n = \frac{n'(p-f)}{p}$.

One example will suffice for showing the simplicity of this formula.

* Biot, Traité de Ph. vol. i. p. 303.

Having 100 measures of air saturated with watery vapour at 60° F. the barometer standing at 30 inches, how many measures would the air occupy if quite dry? $n' = 100$; $p = 30$; $f = 0.524$, the tension of watery vapour at 60°, according to Mr Dalton's table. Hence $n = \frac{100 \times (30 - 0.524)}{30} = \frac{100 \times 29.476}{30} = 98.25$ which is the answer required.

The presence of watery vapour in the atmosphere is owing to evaporation. All the accumulations of water upon the surface of the earth are subjected by its means to a natural distillation; the impurities with which they are impregnated remain behind, while the pure vapour ascends into the air, gives rise to a multitude of meteorological phenomena, and after a time descends again upon the earth. As evaporation goes on to a certain extent even at low temperatures, it is probable that the atmosphere is never absolutely free from vapour.

The quantity of vapour present in the atmosphere is very variable, in consequence of the continual change of temperature to which the air is subject. But even when the temperature is the same, the quantity of vapour is still found to vary; for the air is not always in a state of saturation. At one time it is excessively dry, at another it is fully saturated; and at other times it varies between these extremes. This variable condition of the atmosphere as to saturation is ascertained by the hygrometer.

A great many hygrometers have been invented; but they may all be referred to three principles. The construction of the first kind of hygrometer is founded on the property possessed by some substasnce of expanding in a humid atmosphere, owing to a deposition of moisture within them; and of parting with it again to a dry air, and in consequence contracting. Almost all bodies have the power of attracting moisture from the air, though in different proportions. A piece of glass or metal weighs sensibly less when carefully dried, than after exposure to a moist atmosphere; though neither of them is dilated, because the water cannot penetrate into their interior. Dilatation from the absorption of moisture appears to depend on a deposition of it within the texture of a body, the particles of which are moderately soft and yielding. The hygrometric property therefore belongs chiefly to organic substances, such as wood, the beard of corn, whalebone, hair, and animal membranes. Of these, none is better than the human hair, which not only elongates freely from imbibing moisture, but, by reason of its elasticity, recovers its original length on drying. The hygrometer of Saussure is made with this material.

The second kind of hygrometer points out the opposite states of dryness and moisture by the rapidity of evaporation. Water does not evaporate at all when the atmosphere is completely saturated with moisture; and the freedom with which it goes on at other times, is in proportion to the dryness of the air. The hygrometric condition of the air may be determined, therefore, by observing the rapidity of evaporation. The most convenient method of doing this, is by covering the bulb of a thermometer with a piece of silk or linen, moistening it with water, and exposing it to the air. The descent of the mercury, or the cold produced, will correspond to the quantity of vapour formed in a given time. Mr Leslie's hygrometer is of this kind.

The third kind of hygrometer is on a principle entirely different from the foregoing. When the air is saturated with vapour, and any colder body is brought into contact with it, a deposition of moisture imme-

diately takes place on its surface. This is often seen when a glass of cold spring water is carried into a warm room in summer; and the phenomenon is witnessed during the formation of dew, the moisture appearing on those substances only which are colder than the air. The degree indicated by the thermometer when dew begins to be deposited, is called the *dew-point*. If the saturation is complete, the least diminution of temperature is attended with the formation of dew; but if the air is dry, a body must be several degrees colder before moisture is deposited on its surface; and indeed the dryer the atmosphere, the greater will be the difference between its temperature and the dew-point. Attempts were made to estimate the hygrometric state of the air on this principle by the Florentine Academicians, but the first accurate method was introduced by M. le Roi, and since adopted by Mr Dalton. It consists simply in putting cold water into a glass vessel, the outside of which is carefully dried, and marking the temperature of the liquid at which dew begins to be deposited on the glass. The water when necessary is cooled either by means of ice or a freezing mixture. This method, when carefully performed, is susceptible of great precision.

The hygrometer of Mr Daniell, described in his Meteorological Essays, acts on the same principle. It consists of a cryophorus, as described at page 60, but modified somewhat in form, and containing ether instead of water. Within one of its balls is fixed a delicate thermometer, the bulb of which is partially immersed in the ether so as to indicate its temperature, and the other ball is covered with muslin. When the instrument is used, the muslin is moistened with ether, and the cold produced by its evaporation condenses the vapour within the cryophorus, and causes the ether to evaporate rapidly in the other ball. The cold thus generated chills the ether itself and the ball containing it; and in a short time its temperature descends so low, that dew is deposited on the surface of the glass. As soon as this takes place, the temperature is observed by the thermometer.

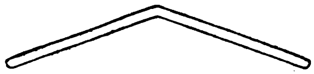
The same object is attained in a still easier way by means of a contrivance described by Mr Jones of London, in the Philos. Trans. for 1826, and soon after in the Edin. Philos. Journal, No. xvii. p. 155, by Dr Coldstream of Leith. It consists of a delicate mercurial thermometer, with its bulb made of thin black glass, about three-fourths of which are covered with muslin. On moistening the muslin with ether the temperature of the bulb and mercury falls, and the uncovered portion of the bulb is soon rendered dim by the deposition of moisture. The temperature indicated at that instant by the thermometer is the dew-point. It appears from some remarks of Mr Daniell in the Quarterly Journal of Science, that this hygrometer was originally invented in Germany, so that Mr Jones and Dr Coldstream are second inventors. Mr Daniell considers the instrument inaccurate, believing that, as the ether is applied to a part only of the bulb, the mercury within will be cooled unequally; that the portion corresponding to the covered part of the bulb will be colder than the mercury opposite to the exposed part, and consequently the dew-point will appear lower than it ought to be. This objection certainly applies when the muslin is rendered very moist with ether, and the temperature of the bulb rapidly reduced; but when the cooling is slowly effected, I believe the indications of this hygrometer to be at least equally correct as those afforded by the very elegant, yet more costly and less portable, apparatus of Mr Daniell. For facts confirmatory of this opinion the reader may consult an essay in the Edinburgh Journal of Science, No. xiii. p. 36, by Mr Foggo, Junr. of Leith.

It is desirable, on some occasions, not merely to know the hygrometric condition of air or gases, but also to deprive them entirely of their vapour. This may be done to a great extent by exposing them to intense cold; but the method now generally preferred is by bringing the moist gas in contact with some substance which has a powerful chemical attraction for water. Of these none is preferable to the chloride of calcium.

## *Constitution of Gases with respect to Caloric.*

The experiments of Mr Faraday on the liquefaction of gaseous substances appear to justify the opinion that gases are merely the vapours of extremely volatile liquids. Most of these liquids, however, are so volatile, that their boiling point, under the atmospheric pressure, is lower than any natural temperature; and this is the reason why they are always found in the gaseous state. By subjecting them to great pressure, their elasticity is so far counteracted that they become liquid. But even when thus compressed, a very moderate heat is sufficient to make them boil; and on the removal of pressure they resume the elastic form, most of them with such violence as to cause a report like an explosion, and others with the appearance of brisk ebullition. An intense degree of cold is produced at the same time, in consequence of caloric passing from a sensible to an insensible state.

The process for condensing the gases (Philos. Trans. for 1823) consists in exposing them to the pressure of their own atmospheres. The materials for producing them are put into a strong glass tube, which is afterwards sealed hermetically, and bent in the middle, as represented by the figure. The gas is generated, if necessary by the appli-



cation of heat, and when the pressure becomes sufficiently great, the liquid is formed and collects in the free end of the tube, which is kept cool to facilitate the condensation. Most of these experiments are attended with danger from the bursting of the tubes, against which the operator must protect himself by the use of a mask.

The pressure required to liquefy the gases is very variable, as will appear from the following table. The results were obtained by Mr Faraday.

| | | |
|---|---|---|
| Sulphurous acid gas . | 2 atmospheres at | 45° F. |
| Sulphuretted hydrogen gas | 17 . . | 50°. |
| Carbonic acid gas . | 36 . . | 32°. |
| Chlorine gas . | 4 . . | 60°. |
| Nitrous oxide gas . | 50 . . | 45°. |
| Cyanogen gas . | 3.6 . . | 45°. |
| Ammoniacal gas . | 6.5 . . | 50°. |
| Muriatic acid gas . | 40 . . | 50°.* |

* The general law in regard to the elasticity or tension of gases is that this property increases with the compressing force. Oersted, however, has shown, that this law does not always hold; for he ascertained that condensable gases, subjected to a pressure near to that at which their condensation would take place, undergo a greater diminu-

## *Sources of Caloric.*

The sources of caloric may be reduced to six. 1. The sun. 2. Combustion. 3. Electricity. 4. The bodies of animals during life. 5. Chemical action. 6. Mechanical action. All these means of procuring a supply of caloric, except the last, will be more conveniently considered in other parts of the work.

The mechanical method of exciting caloric is by friction and percussion. When parts of heavy machinery rub against one another, the heat excited, if the parts of contact are not well greased, is sufficient for kindling wood. The axle-tree of carriages has been burned from this cause, and the sides of ships are said to have taken fire by the rapid descent of the cable. Count Rumford has given an interesting account of the caloric excited in boring cannon, which was so abundant as to heat a considerable quantity of water to its boiling point. It appeared from his experiments that a body never ceases to give out heat by friction, however long the operation may be continued; and he inferred from this observation that caloric cannot be a material substance, but is merely a property of matter. M. Pictet observed that solids alone produce heat by friction, no elevation of temperature taking place from the mere agitation of fluids with one another. He found that the heat excited by friction is not in proportion to the hardness and elasticity of the bodies employed. On the contrary, a piece of brass rubbed with a piece of cedar wood produced more heat than when rubbed with another piece of metal; and the heat was still greater when two pieces of wood were employed.

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# SECTION II.

## LIGHT.

Light is similar to caloric in many of its properties. They are both emitted in the form of rays, traverse the air in straight lines, and are subject to the same laws of reflection. The intensity of each diminishes as the square of the distance from their source. They often accompany each other; and on some occasions seem to be actually converted into one another. It has been supposed, from this circumstance, that they are modifications of the same agent; and though most persons regard them as independent principles, yet they are certainly allied in a way which is at present quite inexplicable.

There are two kinds of light, natural and artificial; the former proceeding from the sun and stars, the latter from bodies which are strongly heated. The light derived from these sources is so different, that it is necessary to speak of them separately.

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tion of volume than is proportional to the pressure. Berzelius accounts for this fact by supposing that the close proximity of the molecules of a gas, occasioned by great pressure, brings the particles more completely within the sphere of each other's attraction, and thus counteracts the separating power of the caloric, which he conceives does not act under favourable circumstances, unless the ponderable particles are at a certain distance from each other. (Berzelius, Traité de Chimie, i. 83, 86.) These views have a bearing on the experiments of Mr Faraday, cited in the text. B.

The solar rays come to us either directly, as in the case of sunshine, or indirectly, in consequence of being diffused through the atmosphere, constituting day-light. They pass freely through some solid and liquid bodies, hence called transparent, such as glass, rock-crystal, water, and many others, which, if clear and in moderately thin layers, intercept a portion of light that is quite inappreciable when compared to the quantity transmited. Opake bodies, on the contrary, intercept the rays entirely, absorbing some of them and reflecting others. In this respect, also, there is a close analogy between light and caloric; for every good reflector of the one reflects the other also.

Though transparent substances permit the light to pass through them, they nevertheless exert a considerable influence upon it in its passage. All the rays which fall obliquely are refracted, that is, are made to deviate from their original direction. It was this property of transparent media which enabled Sir Isaac Newton to discover the compound nature of the solar light, and to resolve it into its constituent parts. The substance commonly employed for this purpose is a triangular piece of glass called the *prism*. Its action depends upon the different refrangibility of the seven coloured rays which compose a colourless one. The violet ray suffers the greatest refraction, and the red the least; while the other colours of the rainbow lie between them, disposed in regular succession according to the degree of deviation which they have individually experienced. The coloured figure so produced is called the *prismatic spectrum*, which is always bounded by the violet ray on one side, and by the red on the other.

The prismatic colours, according to the experiments of Sir W. Herschel, differ in their illuminating power. The orange possesses this property in a higher degree than the red; and the yellow rays illuminate objects still more perfectly. The maximum of illumination lies in the brightest yellow or palest green. The green itself is nearly equally bright with the yellow; but from the full deep green, the illuminating power decreases very sensibly. That of the blue is nearly equal to that of the red; the indigo has much less than the blue; and the violet is very deficient. (Phil. Trans. 1800.)

The solar rays, both direct and diffused, possess the property of exciting heat as well as light. This effect takes place only when the rays are absorbed; for the temperature of transparent substances through which they pass, or of opake ones by which they are reflected, is not affected by them. Hence it happens that the burning glass and concave reflector are themselves nearly or quite cool, at the very moment of producing a strong heat by collecting the sun's rays into a focus. The extreme coldness that prevails in the higher strata of the air arises from the same cause. The rays pass on unabsorbed through the atmosphere; and its lower parts would also be intensely cold, did they not receive caloric by communication from the earth.

The absorption of light is much influenced by the nature of the surface on which it falls; and it is remarkable that those substances which absorb radiant non-luminous caloric most powerfully, are likewise the best absorbers of light. But there is one property of surfaces, namely, colour, which has a great influence over the absorption of light, but exceedingly little, if any, over that of pure radiant caloric. That dark coloured substances acquire a higher temperature in the sunshine than light ones, may be inferred from the general preference given to the latter as articles of dress during summer; and this practice, founded on the experience of mankind, has been justified by direct experiment. Dr Hooke, and subsequently Dr Franklin, proved

the fact by placing pieces of cloth of the same texture and size, but of different colours, upon snow, and allowing the sun's rays to fall upon them. The dark coloured specimens always absorbed more caloric than the light ones, the snow beneath the former having melted to a greater extent than under the others; and it was remarked that the effect was nearly in proportion to the depth of shade. Sir H. Davy has more recently examined the subject, and arrived at the same conclusions.

The rays of the prismatic spectrum differ from one another in their heating power as well as in colour. Their difference in this respect was first noticed by Herschel, who was induced to direct his attention to the subject by the following circumstance. In viewing the sun by means of large telescopes through differently coloured darkening glasses, he sometimes felt a strong sensation of heat with very little light, and at other times he had a strong light with little heat,—differences which appeared to depend on the colour of the glasses which he used. This observation led to his celebrated researches on the heating power of the prismatic colours, which were published in the Philosophical Transactions for 1800.

The experiments were made by transmitting a solar beam through a prism, receiving the spectrum on a table, and placing the bulb of a very delicate thermometer successively in the different parts of it. While engaged in this inquiry, he observed not only that the red was the hottest ray, but that there was a point a little beyond the red, altogether out of the spectrum, where the thermometer stood higher than in the red itself. By repeating and varying the experiment, he discovered that the most intense heating power was always beyond the red ray, where there was no light at all; and that the heat progressively diminished in passing from the red to the violet, where it was least. He hence inferred that there exists in the solar beam a distinct kind of ray, which causes heat but not light; and that these rays, from being less refrangible than the luminous ones, deviate in a less degree from their original direction in passing through the prism.

All succeeding experiments confirm the statement of Sir W. Herschel that the prismatic colours have very different heating powers; but they are at variance with respect to the spot at which the heat is at a maximum. Some assert with Sir W. Herschel that it is beyond the red ray; while others, and in particular Professor Leslie, contend that it is in the red itself. The recent observations of M. Seebeck in the Edinburgh Journal of Science, I. 358, appear decisive of the question. He found that the point of greatest heat was variable according to the kind of prism which was employed for refracting the rays. When he used a prism of fine flint glass, the greatest heat was constantly beyond the red. With a prism of crown glass, the greatest heat was in the red itself. When he employed a prism externally of glass, but containing water within, the maximum was neither in the red, nor beyond it, but in the yellow. It is difficult to account for these phenomena, except on the supposition that the different kinds of prisms differ in their power of refracting caloric. These experiments therefore confirm the opinion of Sir W. Herschel, that the sunbeam contains calorific rays, distinct from the luminous ones; and render it highly probable, that the heating effect imputed to the latter, is solely owing to the presence of the former.

It has long been known that the solar light is capable of producing powerful chemical changes. One of the most striking instances of it is its power of darkening the white chloride of silver, an effect which takes place slowly in the diffused light of day, but in the course of

two or three minutes by exposure to the sun-beam. This effect was once attributed to the influence of the luminous rays; but it appears from the observations of Ritter and Wollaston, that it is owing to the presence of certain rays that excite neither heat nor light, and which, from their peculiar agency, are termed *chemical* rays. It is found that the greatest chemical action is exerted just beyond the violet ray of the prismatic spectrum; that the spot next in energy is occupied by the violet ray itself; and that the property gradually diminishes as we advance to the green, beyond which it seems wholly wanting. It hence follows that the chemical rays are still more refrangible than the luminous ones, in consequence of which they are dispersed in part over the blue, indigo and violet, but in the greatest quantity at a point which is even beyond the latter.

The more refrangible rays of light possess the property of rendering steel or iron magnetic. This property was discovered in the violet ray by Dr Morichini of Rome; but as some experimentalists of eminence had repeated the experiments without success, the subject was involved in some degree of uncertainty. The fact, however, has been established by the learned and accomplished Mrs Somerville of London, who in 1826 gave an account of her researches to the Royal Society. Sewing needles were rendered magnetic by exposure for two hours to the violet ray; and the magnetic property was communicated in a still shorter time, when the violet rays were concentrated by a lens. The indigo rays possess the magnetizing power almost to the same extent as the violet; and the blue and green possess the same power, though in a less degree. It is wanting in the yellow, orange and red. Needles were also rendered magnetic by the sun's rays, transmitted through green and blue glass.

The second kind of light is that which is emitted by substances when strongly heated. All bodies begin to emit light when caloric is accumulated within them in great quantity; and the appearance of glowing or shining, which they then assume, is called *incandescence*. The temperature at which solids in general begin to shine in the dark, is betwen 600° and 700° F; but they do not appear luminous in broad daylight, till they are heated to about 1000° F. The colour of incandescent bodies varies with the intensity of the heat. The first degree of luminousness is an obscure red. As the heat augments, the redness becomes more and more vivid, till at last it acquires a full red glow. Should the temperature still continue to increase, the character of the glow changes, and by degrees becomes white, shining with increasing brilliancy as the intensity of the heat augments. Liquids and gases likewise become incandescent when strongly heated; but a very high temperature is required to render a gas luminous, more than is sufficient for heating a solid body even to whiteness. The different kinds of flame, as of the fire, candles and gas light, are instances of incandescent gaseous matter.

All artificial lights are procured by the combustion or burning of inflammable matter. So large a quantity of caloric is evolved during the process, that the body is made incandescent in the moment of being consumed. Those substances are preferred for the purposes of illumination that yield gaseous products when strongly heated, which by becoming luminous while they burn, constitute flame. The light derived from such sources differs from the solar light in being accompanied by free radiant caloric similar to that emitted by a non-luminous heated body. The free radiant caloric may be separated by a screen of moderately thick glass; but the light so purified still heats any body that absorbs it, whence it would appear that it retains some calorific rays

which, like those in the solar beam, accompany the luminous ones in their passage through solid transparent media*. Terrestrial light has been supposed to contain no chemical rays; but the experiments with lime strongly heated by the method of Mr Drummond, have proved that artificial light of great intensity is productive of chemical changes similar to those occasioned by solar light. (Annals of Philosophy, xxvii. 451.)

Light is emitted by some substances at common temperatures, giving rise to an appearance which is called *phosphorescence*. This phenomenon seems owing in some instances to a direct absorption of light which is afterwards slowly emitted. A composition made by heating to redness a mixture of calcined oyster shells and sulphur, known by the name of *Canton's Phosphorus*, possesses this property in a very remarkable degree. It shines so strongly for a few minutes after exposure to light, that when removed to a dark room the hour on a watch may be distinctly seen by it. After some time it ceases to be luminous, but regains the property when exposed during a short interval to light. No chemical change attends the phenomenon.

Another kind of phosphorescence is observable in some bodies when they are strongly heated. A piece of marble, for example, heated to a degree which would only make other bodies red, emits a brilliant white light of such intensity that the eye cannot support its impression.

A third species of phosphorescence is observed in the bodies of some animals, either in the dead or living state. Some marine animals, and particularly fish, possess it in a remarkable degree. It may be witnessed in the body of the herring, which begins to phosphoresce a day or two after death, and before any visible sign of putrefaction has set in. Sea-water is capable of dissolving the luminous matter; and it is probably from this cause that the waters of the ocean sometimes appear luminous at night when agitated. This appearance is also ascribed to the presence of certain animalcules, which, like the glow-worm of this country, or the fire-fly of the West Indies, are naturally phosphorescent.

It is sometimes of importance to measure the comparative intensities of light, and the instrument by which this is done is called a *photometer*. The only photometer which is employed for estimating the relative strength of the sun's light is that of Mr Leslie. It consists of his differential thermometer, with one ball made of black glass. The clear ball transmits all the luminous rays that fall upon it, and therefore its temperature is not affected by them: they are all absorbed, on the contrary, by the black ball, and by heating and expanding the air within, cause the liquid to ascend in the opposite stem. The whole instrument is covered with a case of thin glass, the object of which is to prevent the balls from being affected by currents of cold air. The action of this photometer depends on the heat produced by the absorption of light. Mr Leslie conceives that light when absorbed is converted into heat; but according to the experiments already referred to, the effect must be attributed, not so much to the light itself, as to the absorption of the calorific rays by which it is accompanied.

Mr Leslie recommends his photometer also for determining the relative intensities of artificial light, such as that emitted by candles, oil, or gas. This application of it differs from the foregoing, because the light proceeding from terrestrial sources contains caloric under two

* Mr Powel, in Phil. Trans. for 1825.

forms: one is analogous to that emitted by a body which is not luminous; the other is similar to that which accompanies the solar light. It is presumed that the first form of caloric will not prove a source of error: that these rays are wholly intercepted by the outer case of glass; or that, should a few penetrate into the interior, they will be absorbed equally by both balls, and will therefore heat them to the same extent. It is probable that this reasoning is not wide of the truth; and consequently, the photometer will give correct indications so far as regards the new element—non-luminous caloric. But it is not applicable to lights which differ in colour; for their heating power is out of all proportion to their light. Thus, the light emitted by burning cinders or red-hot iron, even after passing through glass, contains a quantity of calorific rays, which is out of all proportion to the luminous ones; and consequently, they may and do produce a greater effect on the photometer than some lights whose illuminating powers are far greater.

The second kind of photometer is on a totally different principle. It determines the comparative strength of lights by a comparison of their shadows. This instrument was invented by Count Rumford, and is described by him in his Essays. It is susceptible of great accuracy when employed with the requisite care*; but, like the foregoing, its indications cannot be trusted when there is much difference in the colour of the lights. In this case, the best mode of obtaining an approximative result, is by observing the distance from each light at which any given object, as a printed page, ceases to be distinctly visible. The illuminating power of the lights so compared is as the squares of the distance.

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## SECTION III.

### ELECTRICITY.

When certain substances, such as amber, glass, sealing-wax, or sulphur, are rubbed, and then brought near small fragments of paper, cork, or other light bodies, the latter move rapidly towards the former, and adhere during a longer or shorter interval to their surface. If the body which is thus excited by friction is light and freely suspended, it will move towards the substances in its vicinity. After a while the excited body loses its influence; but it may be renewed for any number of times by friction. The movement observed in these instances is attributed to a peculiar kind of attraction, and the unknown cause of this attraction is called *Electricity*, from the Greek word ηλεκτρον amber, because the electric property was first noticed in this substance.

The ancients were aware that amber and the *lyncurium*, (supposed to be our tourmalin,) may be rendered electric by friction; but it was not known that other bodies may be similarly excited until the commencement of the 17th century, when Dr Gilbert of Colchester detected the same property in a variety of other substances. Of those

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* See an Essay on the Construction of Coal Gas Burners, &c. in the Edinburgh Philosophical Journal for 1825.

which he has enumerated in his treatise *de Magnete*, the principal are the diamond, rock crystal, and several of the precious stones, glass, sulphur, mastic, sealing-wax, and resin; and in making this discovery he laid the foundation of the science of Electricity. A few additional facts were noticed during the course of the same century by Boyle, Otto de Guericke, and Dr Wall, and in 1709 Mr Hawkesbee published an account of many curious electrical experiments; but no material progress was made in this department of knowledge till between the years 1729 and 1733, when the discovery of new and important facts by Mr Stephen Grey in this country, and M. Dufay in France, attracted general attention to the subject, and speedily acquired for it the regular form of a science*.

The most important fact established by Mr Grey was the fundamental one, that electricity passes freely along certain substances, and that its progress is more or less entirely arrested by others. M. Dufay, in repeating the experiments of Grey, observed that an electrified substance not only attracts light bodies, but causes them after contact to fly off from its surface as if by a principle of repulsion. This singular phenomenon, which is termed *electrical repulsion*, had been previously noticed by Otto de Guericke, but the merit of original observation seems also justly due to the French philosopher. Dufay likewise noticed that the electricity excited on glass is different from that of resin, and hence inferred the existence of two kinds of electricity, the *vitreous* and *resinous*, the former belonging to glass, and the latter to resin. He established an excellent mode of distinguishing them, by finding that substances possessed of the same kind of electricity always repel each other; and that attraction is as uniformly exerted between substances which are in opposite states of electrical excitement.

Another fact of consequence, relative to the excitement of electricity by friction, was discovered in 1759 by Mr Symmer, (Philos. Trans. li. 340), who found that when two bodies are rubbed together, both are excited, and that one always possesses vitreous and the other resinous electricity. This induced Symmer to modify the doctrine of the two electricities. Dufay conceived the vitreous electricity to be peculiar to some substances and the resinous electricity to others. Symmer, on the contrary, maintained, that bodies in their ordinary unexcited condition contain both kinds of electricity in a state of combination; and as they then neutralize or counteract each other's effects, no electrical phenomena are apparent; that friction produces excitement by separating the two principles; and that excitation continues until that kind of electricity which has been withdrawn is restored.

Dufay's doctrine of the two electricities as modified by Symmer is consistent with all the facts which subsequent observation has brought to light, and is adopted almost universally in France and other parts of the continent. It is found that all substances, when electrified by friction, are thrown into opposite states of excitement; that electrical repulsion is never observed but between bodies similarly electrified; and that electrical attraction is as uniformly owing to the substances possessing different kinds of electricity. For these phenomena, however, Dr Franklin proposed a different explanation, founded on the supposition of there being only one kind of electricity. According to this philosopher, when bodies contain their natural quantity of elec-

* For the historical details, see Priestley's History of Electricity.

tricity, they do not manifest any electrical properties; but they are excited either by its increase or diminution. On rubbing a tube of glass with a woollen cloth, the electrical condition of both substances is disturbed; the former acquires more or is overcharged, the other less than its natural quantity or is undercharged. These opposite states he expressed by the terms *positive* and *negative*, the first corresponding to the vitreous, the second to the resinous electricity of Dufay. Electrical repulsion, according to Franklin, takes place between substances which contain either more or less than their natural quantity; and electrical attraction is only exerted between two bodies, one of which contains more than its natural quantity and the other less. The excess of electricity has a strong tendency to pass from a positively to a negatively excited surface, so as to restore the equilibrium in both; and this always happens either by contact, or from such proximity that the electricity is able to pass from one to the other through the intervening stratum of air. The phenomena of electricity are explicable by both these theories; but as that of Dr Franklin is commonly adopted in Britain, I shall employ it by preference in this treatise.

It has been objected to this hypothesis that it does not account satisfactorily for the repulsion observed between bodies negatively electrified. The separation of two positive electric bodies is easily accounted for by the repulsive power supposed to be exerted among the particles of the electricity accumulated upon them; while substances which are negative, or possess less than their natural quantity of electricity, cannot be influenced by such a power, and therefore it is argued ought not to diverge or separate. This mode of reasoning, however, is entirely hypothetical. There is no proof that the divergence observed in similarly electrified bodies is owing to actual repulsion; and the phenomenon may be explained equally well on the principle, that the two excited substances are attracted in opposite directions, in consequence of the contiguous strata of air being rendered oppositely electrical by induction. In this way all the phenomena of electrical attraction and repulsion, are referable to the attractive power exerted between bodies in opposite states of excitement. The term repulsion, according to this view, is used merely to express the act of separation or divergence.

Nothing certain is known concerning the principle or cause of the phenomena of electricity. It may possibly be only a property of matter, called into action by particular circumstances; but the phenomena accord much better with the opinion, which is now almost universally received by philosophers, that it is a highly subtile elastic fluid, too light to affect the most delicate balances, capable of moving with extreme velocity, and present in all bodies. Its influence, in excited bodies, is diffused uniformly in every direction; and like light and other principles which are subject to this law, its power diminishes as the squares of the distance. It is one of the most energetic principles in nature. It is the cause of thunder and lightning; the phenomena of galvanism, and probably of magnetism, are produced by it; and the influence which it exerts over chemical changes is so great, that some philosophers regard it as the cause of chemical attraction. The particles of the electric fluid are supposed to be highly repulsive to each other, and to be powerfully attracted by other material substances. The tendency to pass from overcharged surfaces to those that are in a negative state, may be ascribed to one or other of these properties, or perhaps to their conjoint operation.

Electricity may be excited in all solid substances by friction. This

assertion seems at first view contrary to fact. It is well known that a metallic substance, if held in the hand, may be rubbed for any length of time without exhibiting the least sign of electricity; an observation which led to the division of bodies into such as may be excited by friction, and into those that, under the same circumstances, give no sign of electrical excitement. The former were called *Electrics*, the latter *Non-electrics*. But the distinction is not founded in nature. A metallic substance does not indeed exhibit any trace of electricity when rubbed in the same way as a piece of glass; but if, while it is rubbed with the dry fur of a cat, it is supported by a glass handle, it will then evince signs of electrical excitement.

The difficulty and apparent impossibility of exciting metallic bodies, receives an explanation from the fact observed by Grey, that the electric fluid passes with great facility along the surface of some substances, and with difficulty over that of others; and this discovery has led to the division of bodies into *conductors* and *non-conductors* of electricity. If an excited conductor, such as a metallic wire, be made to communicate with the earth at one of its extremities, the electricity will pass to it from the opposite end in an instant, even though it were several miles in length; so that when the equilibrium is disturbed, it will be at once restored along the whole wire, just as effectually as if every point of it communicated with the ground. But an excited stick of glass or resin is not affected in the same manner; for as electricity does not obtain a free passage along them, the equilibrium is restored in those parts only, which are actually touched. For this reason a non-conductor of electricity, though held in the hand, may be readily excited; but a good conducting body cannot be brought into that state, unless it be *insulated*, that is, cut off from communication with the earth by means of some non-conductor. This is generally effected either by supporting a body with a handle of glass, or by placing it on a stool made with glass feet.

To the class of conductors belong the metals, charcoal, plumbago, water, and most substances which contain water in its liquid state, such as animals and plants. The conductibility of these substances is different. Of the metals, according to the experiments of Mr Harris, silver and copper are the best conductors of electricity; then gold, zinc, platinum, iron, tin, and lead. (Philos. Trans. for 1827, Part I. 21.) To the list of non-conductors belong glass, resins, sulphur, the diamond, dried wood, precious stones, silk, hair, and wool. Atmospheric air is also a non-conductor. If it were not so, no substance could retain its electricity when surrounded by it. Aqueous vapour suspended in the air injures the non-conducting property of the latter, and hence electrical experiments do not succeed so well when the air is charged with moisture as when it is dry. The presence of a little moisture communicates conducting properties to the most imperfect conductor; and hence it is impossible to excite glass by rubbing it with a moist substance.

A knowledge of the different conducting power of bodies is required for explaining some circumstances which appear contradictory to a preceding statement. It is above mentioned that when two bodies are excited by friction, they are rendered oppositely electric; but if a tube of glass is rubbed by a person communicating with the ground, the glass will become positively electrical, while the hand of the operator manifests no sign whatever of excitement. The cause of this is obvious. The operator is not electrified, because the earth restores the electric fluid as soon as it is withdrawn by the glass; but if he is insulated, the indications of negative electricity will immediately ap-

pear. Hence it is a rule to insulate a conductor, whenever it is wished to examine its electrical condition.

The experiments which have been made concerning the effects of friction, have demonstrated that the same substance is not always similarly electrified. Its electricity is influenced partly by the state of its surface, and partly by the nature of the body with which it is rubbed. Thus smooth glass is rendered positive by friction with woollen cloth; whereas if its surface is rough, it becomes negative from the same treatment. Smooth glass which is positive with woollen cloth, is rendered negatively electrical by being rubbed with a cat's fur. The following table, from Cavallo's Complete Treatise on Electricity, shows the kind of excitement produced by the friction of various substances.

| | *Is rendered* | *By friction with* |
|---|---|---|
| The back of a cat. | Positive | Every substance with which it has been hitherto tried. |
| Smooth glass. | Positive | Every substance hitherto tried except the back of a cat. |
| Rough glass | Positive | Dry oiled silk, sulphur, and metals. |
| | Negative | Woollen cloth, quills, wood, paper, sealing-wax, white wax, the human hand. |
| Tourmalin | Positive | Amber, a current of air. |
| | Negative | Diamond, the human hand. |
| Hare's skin | Positive | Metals, silk, loadstone, leather, the hand, paper, baked wood. |
| | Negative | Other finer furs. |
| White silk | Positive | Black silk, metals, black cloth. |
| | Negative | Paper, hand, hair, weasel's skin. |
| Black silk | Positive | Sealing-wax. |
| | Negative | The skin of the hare, weasel, and ferret; loadstone, brass, silver, iron, and the hand. |
| Sealing-wax | Positive | Metals. |
| | Negative | The skin of the hare, weasel, and ferret, the hand, leather, woollen cloth, paper. |
| Baked wood | Positive | Silk. |
| | Negative | Flannel. |

Mr Singer states that sealing-wax is not rendered positive by friction with all metals:—iron, steel, lead, and bismuth, as also plumbago, gave it negative. Mr Cavallo's statement with respect to white silk and paper does not agree with my observation. The effect of white paper is variable; but in a number of trials I found that by coarse brown paper white silk was invariably rendered positive.

The foregoing remarks on the effects of friction will render intelligi-

ble the principle of the electrical machine. In the time of Grey a supply of electricity was obtained for experimental purposes by rubbing a glass tube with the dry hand. Glass globes made to revolve by machinery were afterwards substituted for the tube, the friction being at first produced with the hand, and subsequently by means of a fixed rubber. As now constructed the electrical machine is formed either with a cylinder or plate of glass, which is pressed during its rotation by cushions stuffed with hair. The cushion is usually covered with an amalgam of tin and zinc, which, partly by increasing the friction, and partly by the oxidation of the metals, materially assists the action of the machine. The electricity developed on the glass is conducted away by an insulated bar of brass placed close to it, called the *prime conductor*, on which it is collected in considerable quantity. By this means the electricity spread over the whole surface of the prime conductor may be carried off at the same instant, and thus act with far greater power than if accumulated on glass or any other imperfectly conducting substance.

The electricity which is so freely and unceasingly evolved during the action of a good electrical machine, is derived from the great reservoir of electricity, the earth. This is obvious from the fact, that if the whole apparatus is insulated, the evolution of electricity immediately ceases; but the supply is as instantly restored, when the requisite communication is made with the ground. In the state of complete insulation the glass and prime conductor are positive as usual, and the rubber is negatively excited; but as the electricity then developed is derived solely from the machine itself, its quantity is exceedingly small. When the machine is used, therefore, the rubber is made to communicate with the earth. As soon as friction is begun, the glass becomes positive, and the rubber negative; but as the latter communicates with the ground, it instantly recovers the electricity which it had lost, and thus continues to supply the glass with an uninterrupted current. If the rubber is insulated, and the prime conductor communicates with the ground, the electricity of the former and all conductors connected with it, is carried away into the earth, and they are negatively electrified.

Friction is not the only cause of electrical excitement. The electric equilibrium is often disturbed by chemical action; and frequently by the mere contact of two substances of a different kind, as when a plate of zinc is made to touch a plate of copper. The same body is sometimes excited by its different parts being unequally heated. Some substances are excited by mere elevation of temperature. This is noticed in certain crystallized minerals, as in tourmalin, which do not possess that symmetrical arrangement of parts commonly existing in crystals. Electricity is often developed during a change of form. Fused sulphur becomes electrical in cooling, and other liquids exhibit the same appearance in the act of congealing. Evaporation and the condensation of vapour are accompanied by a similar change, and it is probable that the electricity excited by these and other analogous processes is the cause of the electrical phenomena of the atmosphere.

Another cause of excitement is proximity to an electrified body; and as the explanation of many electrical phenomena depends on a knowledge of this fact, it is of importance to understand it clearly. When a substance excited positively is brought near another in its natural state and insulated, the electric equilibrium of the latter is instantly disturbed; the parts nearest to the former become negative, and the distant ones positive. If the body is not insulated, its electricity passes into the earth, and it becomes negatively electrical. If,

on the contrary, the exciting substance is negative, it causes the contiguous parts of a body in its vicinity to become positive. Hence it may be established as a law, that an electrified body tends to produce in contiguous substances an electric state opposite to its own. The electricity developed in this way is said to be *induced*, or to be excited by *induction*. The movement of light bodies towards an excited stick of sealing-wax or glass tube is accounted for on this principle. Thus, the vicinity of the negative sealing-wax renders the surrounding objects positive, and therefore a mutual attraction is exerted. When the inside of a glass bottle is rendered positive by contact with the prime conductor of the electrical machine, the outside, if in communication with the earth, parts with electricity and becomes negative. Both surfaces, therefore, are electrified and are in opposite states; and if a communication be established between them by means of a good conductor, the excess of electricity instantly passes along it, and both sides of the glass return to their natural condition. That the experiment may succeed in the most perfect manner, it is necessary to cover the bottle externally and internally, except to within three or four inches of its summit, with tinfoil, or some other good conductor, in order that every point of both sides of the glass may be brought into communication at the same moment. For without this precaution, the electric equilibrium of the two surfaces of the bottle, owing to the imperfect conducting power of glass, will be restored on those points only which are touched. The apparatus thus described is much employed by electricians, and has received the name of Leyden phial, in consequence of its remarkable effects having been first exhibited at the University of Leyden. To render it more convenient for use, the aperture of the glass jar or phial is closed by some imperfect conductor, such as dry wood, through the centre of which passes a metallic rod that communicates with the tinfoil in the inside of the jar. The phial is electrified or *charged* by holding the outside in the hand, or placing it on the ground, while the metallic rod is made to receive sparks from the prime conductor of an electrical machine. If the jar is insulated, no change will be received, or at least very slight indications of excitement will be manifested. By arranging a number of Leyden phials in a box lined with tinfoil, so that they may all communicate freely by their outer surfaces, and then bringing their inner surfaces into communication by wires, the whole series may be charged and discharged in the same manner as a single phial. This arrangement is known by the name of *electrical battery*.

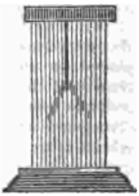
Some of the phenomena of lightning are explained on the principle of induced electricity. When, for instance, a negatively electrified cloud approaches the earth, all objects in its vicinity are positively excited; and when it comes within what is called the *striking distance*, that is, so near that the tendency of the electricity to pass from the positive to the negative body, overcomes the resistance of the intermediate stratum of air, the equilibrium is restored with a report and flash of light, exactly as in the discharge of a Leyden phial. A similar effect is produced by an electrified cloud on other clouds within the sphere of its influence.

The passage of electricity is frequently attended with the production of heat and light, effects which invariably ensue when it meets with an impediment to its progress, as in passing through an imperfect conductor. The most familiar illustration of this is afforded by its passage though the air, when it gives rise to a spark accompanied with a peculiar snapping noise, if in small quantity; or to the phenomena of thunder and lightning, when it takes place on a large scale.

On the contrary, it passes along perfect conductors, such as the metals, without any perceptible warmth or light, provided the extent of their surface is in proportion to the quantity of electricity to be transmitted by them; but if the charge is too great in relation to the extent of the conducting surface, an intense degree of heat will be produced.

Electricity acts with surprising energy on the animal system. When a large quantity of the electric fluid passes through the body, the vital functions cease on the instant, as is exemplified by the numerous accidents on record of persons being killed by lightning. Even the small quantity of electricity contained in a Leyden phial gives a very powerful shock, exciting a sudden spasm of the muscles along which it passes, so violent as to produce a disagreeable or even painful sensation. The shock from a large electrical battery is much more severe, and smaller animals, such as rabbits and fowls, are destroyed by its action.

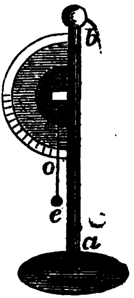
It is very important, in conducting electrical experiments, to possess an easy method of discovering when any substance is electrified, of ascertaining its *intensity* or the degree to which it is excited, and distinguishing the kind of excitement. The mode of effecting these objects is founded on electrical attraction and repulsion, and the instruments employed for the purpose are called *Electroscopes* and *Electrometers*, the latter denoting the intensity of electricity, the former merely indicating excitement, and the electrical state by which it is produced. The term electrometer, however, is often indiscriminately applied to all such instruments, since the methods of ascertaining the kind of excitement give at the same time some idea of its intensity. A body is known to be excited by its power of attracting light substances, and a small ball made of the pith of elder, suspended on a silk thread, affords a convenient material for the experiment. Another mode of acquiring the same information is by means of two pith balls suspended from the same point by silk threads of equal length. When all the surrounding objects are unexcited, the pith balls remain in contact; but on the approach of any electrified body, the two balls are excited by induction, and, having the same electricity, diverge or retreat from each other. A more delicate contrivance, but of a similar kind, was invented by Mr Bennett, and is known by the name of the *Gold Leaf Electrometer*. It consists essentially of a cylindrical glass bottle, with its aperture closed by a brass plate, from the centre of which two slips of gold leaf, are suspended. The brass plate, with its slips of gold leaf, are thus insulated, and the latter prevented from being moved by currents of air by the glass with which they are surrounded. The approach of any electrified body, even though feebly excited, to the brass plate, is immediately detected by the divergence of the leaves. In the annexed wood-cut this electrometer is exhibited with its leaves in a state of divergence.



A very simple method of distinguishing the kind of excitement is the following. If a piece of white silk be drawn a few times rapidly between the fingers, it will become negative; and if in this state it is suspended in the air, it will be attracted by a body positively excited, and repelled by one which is negative. When rubbed on black cloth the silk is rendered positive, and will then of course retreat from a substance similarly electrified, and be attracted by one in an opposite state. The indications of the gold leaf electrometer are still more deli-

cate. If the leaves are diverging with positive electricity, the approach of a positively excited body to the brass plate increases the divergence; because the electric equilibrium is immediately disturbed, and while the plate becomes negative, the gold leaves acquire a still greater degree of electricity. The approach of a negatively excited body would of course be productive of a change precisely opposite, and the divergence, if produced by positive electricity, would be diminished, or even entirely destroyed. To prepare the electrometer for an observation, it is however necessary to communicate to it a known state of excitement. This may be done by touching the electrometer with an electrified body, such as an excited glass tube or stick of sealing-wax, when the whole metallic surface of the electrometer is electrified in the same manner as the substance by which it was touched. A more convenient method is to communicate electricity permanently by induction. Thus, on placing a negatively excited body, as for example a stick of sealing-wax after friction on woollen cloth, near the brass plate of the electrometer, the electric equilibrium of its whole metallic surface is disturbed; the brass plate becomes positive, and the slips of gold leaf diverge from being negative. On withdrawing the sealing-wax, the excess of electricity accumulated on the plate returns to the leaves, and the equilibrium is restored; but if, while the sealing-wax is near the top of the instrument, the plate is touched with the finger, a portion of electricity is supplied to the gold leaves from the earth, and the divergence ceases more or less completely, while the excess of electricity is preserved on the plate by the vicinity of the sealing-wax. On removing *first* the finger and *then* the sealing-wax, the brass is left with an excess of electricity, which extends over the whole metallic surface of the electrometer, and thus produces a divergence which continues for a considerable time, if the glass is dry, and the atmosphere moderately free from moisture.

The electrometer most frequently employed for estimating the intensity of electricity is that shown in the annexed wood cut, invented by Mr Henley, and commonly called the *quadrant electrometer*. It consists of a smooth round stem of wood *a b*, about seven inches long, terminated above by a ball, immediately below which, and projecting from the side of the stem, is attached a semicircular piece of ivory. In the centre *c* of the semicircle is fixed a pin, from which is suspended, to serve as an index, a slender piece of wood or cane *d e*, four inches in length, and terminated by a small ball. When the apparatus is screwed on the prime conductor, or placed on any electrified body, it indicates the intensity of the electricity by the extent to which the index is repelled by the stem. In order to mark the divergence accurately, the lower half of the semicircle, which is traversed by the index, is divided into 90 equal parts or degrees. But this instrument is not well adapted to researches of delicacy. The only electrometer suited for such purposes is the electrical balance invented by Coulomb, which measures the intensity of an excited body by its power of twisting a thread of silk or a fine metallic wire.




In some of the preceding remarks a term has been employed, which perhaps will not be understood without an explanation. By electric *tension* or *intensity* is meant that state of a body which is estimated by an electrometer. When a body acts feebly on the electrometer its intensity is low, and it differs but little from its natural state; and

on the contrary if it affects the electrometer powerfully, its electric tension is great. The higher the intensity of a body, the more it is removed from its natural state, and the greater its tendency to return to an equilibrium. *Intensity* is distinct from *quantity* of electricity. That intensity is not dependent on quantity alone, is proved by the tension of a charged Leyden phial being equal to that of a large battery containing twenty times more electricity. The tension appears to depend on the quantity of electricity accumulated or deficient in a given space; so that the intensity of those substances is greatest, which have the greatest excess or deficiency of electricity in proportion to their surface.

Electricity appears to diffuse itself over the surface of bodies, and the quantity contained on the same substance, all other circumstances being the same, depends on the extent of surface, and is not connected with quantity of matter. Thus a solid sphere of brass cannot contain more electricity than a hollow sphere of the same diameter.

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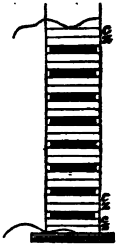
## SECTION IV.

### GALVANISM.

The science of Galvanism owes its name and origin to the experiments on animal irritability made by Galvani, Professor of Anatomy at Bologna, in the year 1790. In the course of the investigation he discovered the fact, that muscular contractions are excited in the leg of a frog recently killed, when two metals, such as zinc and silver, one of which touches the crural nerve, and the other the muscles to which it is distributed, are brought into contact with one another. Galvani imagined that the phenomena are owing to electricity present in the muscles, and that the metals only serve the purpose of a conductor. He conceived that the animal electricity originates in the brain, is distributed to every part of the system, and resides particularly in the muscles. He was of opinion that the different parts of each muscular fibril are in opposite states of electrical excitement, like the two surfaces of a charged Leyden phial, and that contractions take place whenever the electric equilibrium is restored. This he supposed to be effected during life though the medium of the nerves, and to have been produced in his experiments by the intervention of metallic conductors.

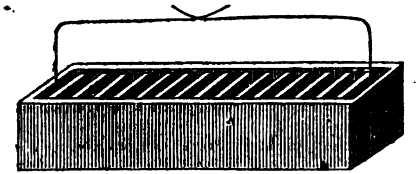
The views of Galvani had several opponents, one of whom, the celebrated Volta, Professor of Natural Philosophy at Pavia, succeeded in pointing out their fallacy. Volta maintained that the electricity is excited by the contact of the metals; that the animal substances merely act as conductors in restoring the electric equilibrium at the moment of its being disturbed; and that the contraction is produced by the stimulus arising from the passage of electricity along the nerves and muscular fibres. He proved that electricity is excited in the way he supposed, by bringing plates of different metals, such as zinc and silver, in contact with one another, and examining their electrical state at the moment of separation by means of a delicate electrometer. For this purpose, it is necessary to insulate each of the metallic discs, by supporting them on a handle of glass or resin. On taking this precaution, it was found that both the metals are excited, the silver negatively, and the zinc positively.

As the quantity of electricity excited by any two metals is small, Volta endeavoured to increase the effect by employing several pairs of metals, connecting them in such a manner that the electricity excited by each pair should be diffused through the whole series; and this attempt led him to the construction of the Voltaic pile, a description of which was published in the Philosophical Transactions for 1800. It consists of any number of pairs of zinc and copper, or zinc and silver plates, each pair being separated from the adjoining ones by pieces of cloth, nearly of the same size as the plates, and moistened in a saturated solution of salt. The relative position of the metals in each pair must be the same in the whole series; that is, if the copper is placed below the zinc in the first combination, the same order must be preserved in all the others. The pile, as shown in the figure is contained in a proper frame, formed of glass pillars, fixed into a piece of thick wood, which both supports and insulates it.



The apparatus so formed is in the same state of excitement as the insulated metallic discs after contact, and affects the electrometer and excites muscular contractions in a similar manner, but in a much greater degree. The opposite ends of the pile are also differently excited, the side which begins with a zinc plate being positive and the other negative; and hence when they are made to communicate by means of a good conductor, electricity must pass from the one to the other, precisely as is supposed to happen in the discharge of a Leyden phial. But the apparatus is not thereby rendered inactive; for as the conditions which originally excited it are still maintained, the equilibrium is no sooner restored than it is again disturbed, and therefore a continued current must pass from one end or pole to the other along the wire by which they are connected.

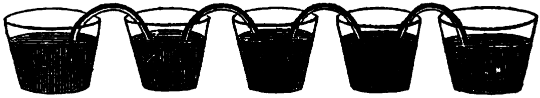
The Voltaic pile is now rarely employed, because we possess other modes of forming galvanic combinations which are far more powerful and convenient. The galvanic battery, proposed by Mr Cruickshank, and represented in the annexed cut, consists of a trough of baked



wood, about thirty inches long, in which are placed at equal distances, fifty pairs of zinc and copper plates previously soldered together, and so arranged that the same metal shall always be on the same side. Each pair is fixed in a groove cut in the sides and bottom of the box, the points of junction being made water-tight by cement. The apparatus thus constructed is always ready for use, and is brought into action by filling the cells left between the pairs of plates with some convenient solution, which serves the same purpose as the moistened cloth in the pile of Volta.

Other modes of construction are now in use which facilitate the employment of the galvanic apparatus, and increase its energy. The trough, made either of baked wood or glazed earthenware, is divided

into partitions of the same material. Each cell contains a plate of zinc and another of copper, which do not touch each other, but communicate merely through the medium of the fluid in which they are immersed. The zinc plate of one cell is connected with the copper of the adjoining one by means of a slip of copper. All the plates are attached to a piece of wood, and may thus be introduced into the liquid of the trough, or removed from it at pleasure. This method was suggested by the *Couronne de Tasses* of Volta, an arrangement which was described by him, together with his pile, in the paper already alluded to. It consists of cups or glasses placed in a line, and containing the fluid for exciting the plates. Each glass, except the extreme ones, contains a plate of zinc, Z, and a plate of copper or silver, C; and each zinc plate is attached to the copper of the adjoining glass by a metallic wire, as represented in the figure.



In batteries of this construction the development of electricity is not produced by direct contact, but by the proximity of the plates while separated by an imperfect conductor. The connection between the zinc of one cell and the copper of the adjoining one, is to afford a passage for electricity from one member of the series to another. An additional improvement was suggested by Dr Wollaston, (see Mr Children's paper in the Philos. Trans. for 1815), who recommends that each cell shall contain one zinc and two copper plates, so that both surfaces of the first metal may be opposed to one of the second. In consequence of this arrangement, the plates of copper communicate with each other, and the zinc between them with the copper of the adjoining cell. An increase of one half the power is said to be obtained by this method.

The size and number of the plates may be varied at pleasure. The largest battery ever made is that of Mr Children, described in the paper above referred to, the plates of which are six feet long, and two feet eight inches broad. The common and most convenient size for the plates is four or six inches square; and when great power is required, a number of different batteries are united by establishing a metallic communication between the positive pole of one battery and the negative pole of the adjoining one. The great battery of the Royal Institution is composed of 2000 pairs of plates, each plate having 32 square inches of surface. It was by this that Sir H. Davy was enabled to effect the decomposition and determine the constitution of the alkalies, a discovery which has at once extended so much the bounds of chemical science, and conferred immortal honour on the name of the discoverer.

When a Voltaic battery is in operation, chemical changes always occur between the liquid of the cells, and one of the metals with which it is in contact. And these changes have been observed to be so constant, and so intimately associated with some of the most remarkable effects of the pile, that they have been thought by some philosophers to be essential to the phenomena of galvanism. In favour of this opinion very strong arguments have been adduced. The energy of a battery in producing chemical decomposition certainly depends on the nature of the liquid contained in its cells. Thus when

they are filled with pure water, the decomposing power is very feeble; but even then the surface of the zinc is gradually corroded. A saline solution increases the chemical energy of the battery, and at the same time the oxidation of the zinc is more rapid than with pure water. An acid corrodes the zinc with still greater rapidity, and proportionally augments the power of the battery in effecting decomposition. It is established, however, that the electrical effects are not proportional to the chemical changes going on in the battery; and it is a question, which will be considered in the sequel of this section, how far these phenomena are necessarily connected with each other.

In constructing a galvanic battery, each member of the series must consist either of one imperfect and two perfect conductors, or of one perfect and two imperfect. In his Bakerian Lecture for 1826* Sir H. Davy has given the following list of the first kind of Voltaic arrangements, the imperfect conductor being either the common acids, alkaline solutions, or solutions of the hydrosulphurets. The metal first mentioned is positive to all those below it in the scale.

*With common Acids.*

Potassium and its amalgams, barium and its amalgams, amalgam of zinc, zinc, amalgam of ammonium? cadmium, tin, iron, bismuth, antimony? lead, copper, silver, palladium, tellurium, gold, charcoal, platinum, iridium, rhodium.

*With Alkaline Solutions.*

The alkaline metals and their amalgams, zinc, tin, lead, copper, iron, silver, palladium, gold, platinum, &c.

*With Solutions of Hydrosulphurets.*

Zinc, tin, copper, iron, bismuth, silver, platinum, palladium, gold, charcoal.

The following table of Voltaic arrangements of the second kind is from Sir H. Davy's Elements of Chemical Philosophy:

*Table of some Electrical Arrangements, consisting of one Conductor and two imperfect Conductors.*

| | | |
|---|---|---|
| Solution of Sulphur and Potassa | Copper | Nitric Acid |
| Potassa | Silver | Sulphuric Acid |
| Soda | Lead | Muriatic Acid |
| | Tin | Any solution containing Acid. |
| | Zinc | |
| | Other Metals | |
| | Charcoal | |

In all combinations in which the fluids act chemically by affording oxygen, the positive pole is always attached to the metal which has the strongest affinity for oxygen; but when the fluid menstrua afford sulphur to the metals, the metal which has the strongest affinity for sulphur will be positive. Thus, in a series of copper and iron plates introduced into a porcelain trough, the cells of which are filled with water or acid solutions, the iron is positive, and the copper negative; but when the cells are filled with solution of sulphur and potassa, the copper is positive, and the iron negative.

* Philosophical Transactions for 1826. Part iii.

In all combinations in which one metal is concerned, the surface opposite to the acid is negative, and that in contact with the solution of alkali and sulphur, or of alkali, is positive. (Elements of Chemical Philosophy.)

The more remarkable effects of the galvanic battery may be conveniently considered under three heads. 1st, Its electrical effects; 2d, its chemical agency; and 3d, its action on the magnet.

I. Under the first head are included all those effects of the battery which resemble the usual phenomena produced by the electrical machine. When a wire attached to the zinc or positive side of a Voltaic battery is made to communicate with Bennett's electrometer, the gold leaves diverge with positive electricity, and a wire from the negative side produces an effect precisely opposite. But in order that these phenomena should ensue, the two wires must not touch each other; for in that case an electric current would be established along the wires, and the tension cease. When wires connected with the opposite poles or sides of an active galvanic trough are brought near each other, a spark is seen to pass between them; and on establishing the communication by means of the hands previously moistened, a distinct shock is perceived. These effects are rendered more conspicuous by connecting one of the wires with the inner surface, and the other with the outside of a Leyden phial or battery, when successive charges will be received, by means of which all the ordinary electrical experiments may be exhibited. On connecting the opposite ends of a sufficiently powerful battery by means of fine metallic wires or slender pieces of charcoal, these conductors become intensely heated, the wires even of the most refractory metals are fused, and a vivid white light appears at the points of the charcoal, equal if not superior in intensity to that emitted during the burning of phosphorus in oxygen gas; and as this phenomenon takes place in an atmosphere void of oxygen, or even under the surface of water, it manifestly cannot be ascribed to combustion. If the communication be established by metallic leaves, the metals burn with vivid scintillations. Gold leaf burns with a white light tinged with blue, and yields a dark brown oxide; and the light emitted by silver is exceedingly brilliant, and of an emerald green colour. Copper emits a bluish white light attended with red sparks, lead a beautiful purple light, and zinc a brilliant white light inclining to blue, and fringed with red. (Singer.) The properties above enumerated naturally give rise to the belief, that the agent or power exited by the Voltaic apparatus is identical with that which is called into activity by the electrical machine; and the arguments in favour of this opinion seem quite satisfactory. For not only may all the common electrical experiments be performed by means of galvanism, but it has been shown by Dr Wollaston (Phil. Trans. for 1801) that the chemical effects of the galvanic battery may be produced by electricity.

The conditions required for producing the electrical effects of the Voltaic battery are different. Some phenomena are dependent altogether on the electric intensity of the apparatus; for others both quantity and intensity are essential; and for the production of other effects the passage of a large quantity of electricity is alone required. The electric tension of a battery depends chiefly on the number of the series, and comparatively little either on the size of the plates, or the fluid by which they are excited; whereas all these conditions have a material influence over the quantity of electricity. When it is wished to procure a high degree of tension, a great number of small plates

should be employed, and the cells filled with water. On the contrary, when quantity of electricity is the chief object, great extent of surface is necessary: the individual plates should be of large size, and excited by an acid, which promotes the object, partly by producing brisk chemical action, and partly by serving as a more perfect conductor than water or solutions of neutral salts.

Since the force of electrical attraction and repulsion arises from intensity independent of quantity of electric fluid, it is manifest that an electrometer is affected solely by the tension of a battery, and serves as a measure of its degree. For acting on the electrometer, therefore, a battery of numerous small plates is peculiarly suited; their size need not exceed an inch or two inches square. Mr Singer, in his Treatise on Electricity and Galvanism, stated, that common river water is the best material for exciting a battery of this kind, and that the addition of saline or acid matter even diminishes the intensity. He found that an apparatus so charged will retain its activity for months.

For producing sparks, charging an electrical battery, or giving shocks, both tension and quantity of electricity are desirable: and the apparatus designed for such purposes should have a numerous series of plates about four inches square, and be excited with dilute acid. In burning metallic leaf, fusing wire, and igniting charcoal, a large quantity of electricity is the only requisite. The phenomena seem to arise from the electricity passing along these substances with difficulty; a circumstance which, as perfect conductors are used, can only happen when the quantity to be transmitted is out of proportion to the extent of surface over which it has to pass. It is therefore an object to excite as large a quantity of electricity in a given time as possible, and for this purpose a few large plates answer better than a great many small ones. A strong acid solution should also be used; for an energetic action, though of short duration, is more important than a moderate one of greater permanence. A mixture of fourteen or sixteen parts of water to one of nitrous acid is applicable; or for the sake of economy, a mixture of one part of nitrous to two parts of sulphuric acid may be substituted for pure nitrous acid. The large battery of Mr Children, though capable of fusing several feet of platinum wire, had an electric tension so feeble, that it did not affect the gold leaves of the electrometer, gave a shock scarcely preceptible even when the hands were moist, communicated no charge to a Leyden phial, and could not produce chemical decomposition*.

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* Dr Hare has broached a very ingenious theory to account for the heat excited by galvanic action. He does not consider it probable that the heat extricated by galvanic combinations is the effect of the current of electricity passing with difficulty along conductors, in consequence of the quantity to be transmitted being out of proportion to the extent of the surfaces over which it has to pass. On the contrary, he believes that caloric, like electricity, is an *original* product of galvanic action. According to his views, the relative proportion of the two principles evolved depends upon the construction of the apparatus, the caloric being in proportion to the extent of the generating surface, and the electricity to the number of the series. In the case of batteries, in which the size and number of the plates are very considerable, both electricity and caloric are presumed by him to be generated in large quantities. When the number of the plates is very great, and their size insignificant, as in De Luc's column, electricity is the

II. The chemical agency of the Voltaic apparatus, to which chemists are indebted for their most powerful instrument of analysis, was discovered by Messrs Carlisle and Nicholson, soon after the invention was made known in this country. The substance first decomposed by it was water. When two gold or platinum wires are connected with the opposite poles of a battery, and their free extremities are plunged into the same cup of water, but without touching each other, hydrogen gas is disengaged at the negative wire, and oxygen at the positive side. By collecting the gases in separate tubes as they escape, they are found to be quite pure, and in the exact proportion of two measures of hydrogen to one of oxygen. When wires of a more oxidable metal are employed, the result is somewhat different. The hydrogen gas appears as usual at the negative pole; but the oxygen, instead of escaping, combines with the metal, and converts it into an oxide.

This important discovery led many able experimenters to make similar trials. Other compound bodies, such as acids and salts, were exposed to the action of galvanism, and all of them were decomposed without exception, one of their elements appearing at one side of the battery, and the other at its opposite extremity. An exact uniformity in the circumstances attending the decomposition was also remarked. Thus, in decomposing water or other compounds, the same kind of body was always disengaged at the same side of the battery. The metals, inflammable substances in general, the alkalies, earths, and the oxides of the common metals, were found at the negative pole; while oxygen, chlorine, and the acids, went over to the positive surface.

In performing some of these experiments, Sir H. Davy observed, that if the conducting wires were plunged into separate vessels or water, made to communicate by some moist fibres of cotton or amianthus, the two gases were still disengaged in their usual order, the hydrogen in one vessel, and the oxygen in the other, just as if the wires had been immersed into the same portion of that liquid. This singular fact, and another of the like kind observed by Hisinger and Berzelius, induced him to operate in the same way with other compounds, and thus gave rise to his celebrated experiments on the transfer of chemical substances from one vessel to another, detailed in the Philosophical Transactions for 1807. Two agate cups, N and P,

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sole product; and conversely, where the size is very great and the number of the series small, caloric is abundantly produced, and the electrical effects are nearly null. Following up this idea, Dr Hare constructed an instrument, consisting of very large plates, in which the number, being only one pair, was as small as the nature of the case would admit of, with the expectation that such a construction would generate caloric exclusively. The result answered his expectations, and the instrument, from its peculiar powers, was denominated by the inventor a *Calorimotor* or *mover of heat*. (Hare's Chemical Compendium.—Appendix.) Subsequently Dr Hare constructed another galvanic apparatus of peculiar construction, to which he has affixed the name of *Deflagrator*. This instrument is more powerful than any galvanic arrangement heretofore contrived, not even excepting the great battery of Mr Children. For an account of the effects of this instrument, and the theory of its construction, the reader is referred to Dr Hare's papers, published in Silliman's Journal. B.

were employed in them, the first communicating with the negative, the second with the positive pole of the battery, and connected together by moistened amianthus. On putting a solution of sulphate of potassa or soda into N, and distilled water into P, the acid very soon passed over to the latter, while the liquid in the former, which was at first neutral, became distinctly alkaline. The process was reversed by placing the saline solution in P, and the distilled water in N, when the alkali went over to the negative cup, leaving free acid in the positive. That the acid in the first experiment, and the base in the second, actually passed along the amianthus, was obvious; for on one occasion, when nitrate of silver was substituted for the sulphate of potassa, the amianthus leading to N was coated with a film of metal. A similar transfer may be effected by putting distilled water into N and P, and a saline solution in a third cup placed between the two others, and connected with each by moistened amianthus. In a short time the acid of the salt appears in P, and the alkali in N.

The galvanic action not only separates the elements of compound bodies, but suspends the operation of affinity so entirely as to enable an acid to pass though an alkaline solution, or an alkali through water containing a free acid, without combination taking place between them. The three cups being arranged as in the last experiment, Sir H. Davy put a solution of sulphate of potassa in N, pure water in P, and a weak solution of ammonia in the intermediate cup, so that no sulphuric acid could find its way to the distilled water in P without passing through the ammoniacal liquid on its passage. A battery composed of 150 pairs of 4-inch plates was set in action, and in five minutes free acid appeared at the positive pole. Muriatic and nitric acids were in like manner made to pass through strong alkaline solutions; and on reversing the experiment, alkalies were transmitted directly through acid liquids without entering into combination with them.

The analogy between the preceding phenomena and the attractions and repulsions exerted by ordinary electricity is too close to escape observation. If an acid or an alkali pass from one vessel to another in opposition to gravity and chemical affinity, it is clear that this singular phenomenon must arise from the substance so transferred being under the influence of a still stronger attraction; and the only power to which such an effect can in the present case be attributed, is electricity. Now, in all instances of common electrical attraction, the bodies attract one another in consequence of being in opposite states of excitement; and, in like manner, the tendency of acids towards the zinc, and of alkalies towards the copper extremity of the Voltaic apparatus, can be explained, consistently with our present knowledge, only on the supposition that the former are negatively, and the latter positively electric, at the moment of being separated from one another. To account for the elements of compounds being in such a state, a peculiar hypothesis was advanced by Sir H. Davy, which has received the appellation of the *electro-chemical theory*, and has been adopted by several philosophers, especially by Berzelius. This theory was first developed by its author in 1807 in his essay on *Some Chemical Agencies of Electricity*, and he has lately given an additional explanation of his views in the Bakerian Lecture for 1826. Some parts of the doctrine are unfortunately expressed in a manner somewhat obscure, and this circumstance has

given rise to accidental misrepresentation; but a careful perusal of Sir H. Davy's essays induces me to hope, that the following is a correct statement of his opinions.

It was demonstrated by Volta that the mere contact of certain metals, as for example zinc and copper, causes the development of electricity; for after separation they are found, if insulated, to be oppositely electrified. It is inferred, and I conceive correctly, that the electric equilibrium is disturbed at the moment of contact, and that one metal becomes positively and the other negatively electric; but so long as the contact continues, no sign of electrical excitement is evinced, because the presence of two surfaces oppositely electrified to the same degree, counteracts or neutralizes the effect which either separately would produce. The development of electricity by contact is by no means confined to the metals. Sir H. Davy observed that a dry alkali or alkaline earth is excited positively by contact with a metal, and that dry acids after having touched a metal are negative; and he has further shown that acids and alkalies in their dry state excite each other, the former after contact being negative and the latter positive. A similar disturbance of the electric equilibrium is conceived to be produced by the contact of the ultimate particles or atoms of two bodies, as is developed in the same substances when in mass. The two particles are thus rendered oppositely electric, and if not prevented by cohesion to particles of their own kind or other causes, they remain permanently attached to each other by the force of electrical attraction, and thus give rise to a new compound. What chemists term chemical attraction or affinity is, therefore, under this point of view, an electrical force arising from particles of a different kind attracting each other, in consequence of being in opposite states of electrical excitement. The particles thus adhering or combined retain their electrical state, as happens with two discs of zinc and copper while in contact, without exhibiting any signs of electrical excitement either at the moment of combination, or during its continuance. The very existence of the compound, indeed, depends on its elements retaining their state of excitement; and were they both brought into the same electric condition, or subjected to the influence of surfaces of greater intensity than that by which their union is maintained, decomposition would necessarily ensue. This is precisely the manner in which chemical decomposition is thought to be effected by the agency of galvanism. On immersing the extremities of wires connected with the opposite poles of a Voltaic battery into a cup of water, the wire attached to the zinc being positive will attract the oxygen; and if its intensity exceed that by which the elements of water are held together, the oxygen will be drawn towards it and the hydrogen repelled. The wire connected with the copper or negative side of the apparatus exerts an attraction for the hydrogen, and is repulsive to the oxygen; so that the same element which is repelled by one wire is attracted by the other. Other compounds will of course be liable to decomposition on the same principle*.

* If the explanation here given of the chemical agencies of the Voltaic apparatus were well founded, then it would follow that decomposition should take place, if the same portion of water was placed in connection, at the same time, with the positive pole of one battery and the negative pole of another. Thus the negative oxygen being attracted more strongly by the positive or zinc pole than by the positive

It will appear on a little reflection, that the accuracy of this very ingenious doctrine has not yet been demonstrated. There is no proof that the ultimate particles of bodies do become electric by contact, or that they retain their opposite electricities when combined. Were these points established, it would not necessarily follow that chemical affinity is identical with electrical attraction. Besides, it has not been fully proved, that the chemical agency of the Voltaic apparatus depends on electrical attraction and repulsion. The theory does not yet stand on so firm a basis as to induce chemists to abandon the nomenclature they have hitherto employed, and cease to regard affinity as a distinct species of attraction. But at the same time it must be admitted that the electro-chemical theory is founded, as all theoretical views ought to be, on extensive observation and numerous facts; that it supplies chemists with a principle capable of accounting for the phenomena ascribed to affinity, and affords a consistent explanation of the chemical agencies of the Voltaic apparatus. Experience has shown that it is a safe guide in experimental research, and it has the unquestionable merit of having led to one of the most brilliant discoveries ever made in chemistry.

Regarding all compounds as constituted of oppositely electrical elements, Sir H. Davy conceived that none of them should resist decomposition, if exposed to a battery of sufficient intensity; and he accordingly subjected to galvanic action substances which till then had been regarded as simple, expecting that if they were compound they would be resolved into their elements. The result exceeded expectation. The alkalies and earths were decomposed; a substance with the aspect and properties of a metal appeared at the negative pole, while oxygen gas was disengaged at the positive surface. (Phil. Trans. for 1808.)

The same views have been applied successfully on a very recent occasion. It has been long known that the copper sheathing of vessels oxidizes very readily in sea water, and consequently wastes with such rapidity as to require frequent renewal. Sir H. Davy observed that the copper derived its oxygen from atmospheric air dissolved in the water, and that the oxide of copper then took muriatic acid from the soda and magnesia, forming with it a submuriate of the oxide of copper. Now if the copper did not oxidize, it could not combine with muriatic acid; and according to Sir H. Davy, it only combines with oxygen, because by contact with that body it is rendered positively electrical. If, therefore, the copper could by any means be made negative, then the copper and oxygen would have no tendency to unite. The object then was to render copper permanently negative. Now this is done by bringing copper in contact with zinc or iron; for the former then becomes negative, and the latter positive.

Acting on this idea, it was found that the oxidation of the copper may be completely prevented. A piece of zinc as large as a pea, or

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hydrogen with which it is combined, would have its union with the latter severed, a result which would be favoured by the repulsion exercised by the positive pole on the hydrogen. Again, the positive hydrogen would be attracted by the negative pole and the oxygen be repelled. But I doubt very much whether any decomposition would take place under such circumstances, and hence I believe that a current of the galvanic fluid through compounds is essential to its decomposing powers. B.

the head of a small round nail, was found fully adequate to preserve forty or fifty square inches of copper; and this wherever it was placed, whether at the top, bottom, or middle of the sheet of copper, or under whatever form it was used. And when the connection between different pieces of copper was completed by wires, or thin filaments of the 40th or 50th of an inch in diameter, the effect was the same; every side, every surface, every particle of the copper remained bright, whilst the iron or the zinc was slowly corroded. Sheets of copper defended by 1-40th to 1-1000th part of their surface of zinc, malleable and cast iron, were exposed during many weeks to the flow of the tide in Portsmouth harbour, and their weight ascertained before and after the experiment. When the metallic protector was from 1-40th to 1-150th there was no corrosion nor decay of the copper; with smaller quantities, such as 1-200th to 1-460th, the copper underwent a loss of weight which was greater in proportion as the protector was smaller; and as a proof of the universality of the principle, it was found that even 1-1000th part of cast iron saved a certain proportion of the copper. (Phil. Trans. for 1824.)

Unhappily for the application of this principle in practice, it is found that unless a certain degree of corrosion takes place in the copper, its surface becomes foul from the adhesion of sea-weeds and shell-fish. The oxide and submuriate of copper formed when the sheathing is unprotected, is probably injurious to these plants and animals, and thus preserves the copper free from foreign bodies. It appears also that, in vessels whose sheathing is protected from corrosion, the negatively electric copper attracts the positive electric bodies, such as magnesia and lime, dissolved in sea-water; and that these earths then form a nidus for the adhesion of other matters. It is hoped that by duly adjusting the proportion of iron and copper, a certain degree of corrosion may be allowed to occur, sufficient to prevent the adhesion of foreign bodies, and yet materially retarding the waste of the copper; but the attempts to accomplish so desirable an object have not yet been altogether successful.

These principles may be usefully applied on other occasions. One obvious application of the kind, suggested by Mr Pepys, is to preserve iron or steel instruments from rust by contact with a piece of zinc. The iron or steel is thereby rendered negative, while the zinc, being positive, oxidizes with increased rapidity.

The electro-chemical theory furnishes a scientific principle, perhaps I may be allowed to add the most philosophical which we possess, for the arrangement of chemical substances. Dr Henry has adopted this principle of classification in his Elements of Experimental Chemistry; and my chief reason for not following his example is the opinion, that the order of describing the elementary substances adopted in this treatise is more convenient for the student than an arrangement founded on the electro-chemical theory. According to the method suggested by this doctrine, bodies are divided into groups accordingly as their natural electric energies are the same or different. By the term *natural electric energy* is not meant that a substance considered singly, naturally possesses one kind of excitement rather than another; but that by its nature it is disposed from contact with other bodies, to assume one particular electrical state rather than the other. Thus oxygen is called a negative electric, because it is negatively excited by other bodies; whereas the natural electric energy of potassium is positive, because it acquires an excess of electricity by the action of other substances. The electric ener-

gies are ascertained by exposing compounds to the action of a galvanic battery, and observing the pole, at which the elements appear. Those that collect around the positive pole are said to have a negative electric energy; and those are considered positive electrics which are attracted towards the negative pole. Of the elementary principles, oxygen, chlorine, iodine, and fluorine, to which the newly discovered principle bromine should be added, are regarded by Dr Henry as negative electrics; and all the others compose the more numerous list of positive electrics.

Considerable difficulty arises in the arrangement of some substances, in consequence of their possessing one kind of electric energy in relation to some bodies, and an opposite energy with others. Oxygen is negative in every combination, and potassium appears to be as uniformly positive; but sulphur, though positive with respect to oxygen, is negative in relation to the metals. Hydrogen is highly positive when compared with oxygen, chlorine, and other analogous principles; but with the metals its electric energy is negative.

The following lists, showing the electric energy of the different elementary substances in relation to each other, is taken from Berzelius's System of Chemistry. They are given by the author as an approximation to their true order, rather than as rigidly exact. All the bodies enumerated in the first row are negative to those of the second. In the first column each substance is negative to those below it; and in the second, each element is positive compared with the subsequent ones.

| 1<br>*Negative Electrics.* | 2<br>*Positive Electrics.* |
|---|---|
| Oxygen. | Potassium. |
| Sulphur. | Sodium. |
| Nitrogen. | Lithium. |
| Chlorine. | Barium. |
| Iodine. | Strontium. |
| Fluorine. | Calcium. |
| Phosphorus. | Magnesium. |
| Selenium. | Glucinium. |
| Arsenic. | Yttrium. |
| Chromium. | Aluminium. |
| Molybdenum. | Zirconium. |
| Tungsten. | Manganese. |
| Boron. | Zinc. |
| Carbon. | Cadmium. |
| Antimony. | Iron. |
| Tellurium. | Nickel. |
| Columbium. | Cobalt. |
| Titanium. | Cerium. |
| Silicium. | Lead |
| Osmium. | Tin. |
| Hydrogen. | Bismuth. |
| | Uranium. |
| | Copper. |
| | Silver. |
| | Mercury. |
| | Palladium. |
| | Platinum. |
| | Rhodium. |
| | Iridium. |
| | Gold. |

For exhibiting the chemical agency of galvanism, a combination of quantity and intensity is required. The larger of the two immense batteries constructed by Mr Children had scarcely any power in effecting chemical decomposition; and a series of numerous small plates charged with water, and capable of acting powerfully on the electrometer, decomposes water very feebly. The most appropriate apparatus for chemical purposes, is one made with a considerable number of plates of four or six inches square. An acid solution should be employed for exciting the battery, and its strength such as to cause a moderate, long continued action, rather than a violent one of short duration. Any of the stronger acids, such as the nitric, sulphuric, or muriatic, may be used with this intention; but the last, according to Mr Singer, produces the most permanent effect, and is therefore preferable. The proportion should be one part of acid to about 14 or 20 parts of water; or if the series is extensive, the acid may be still further diluted with advantage. The chemical agency of a battery increases with the number of plates; but the exact rate of increase has not been satisfactorily determined.

In order that chemical decomposition should take place by means of galvanism, the compound subjected to its action must be made to connect the opposite poles of the battery. No effect is produced if a non-conductor is used, and hence potassa is not decomposed by galvanism, unless slightly moistened; nor must the electric fluid pass through it with the same facility as along a metal, for the apparatus is then equally inert. The substance by which the opposite poles are connected must be what is called an imperfect conductor, such as water, and saline and acid solutions. All such liquids may be considered perfect conductors in respect to common electricity; but to electrified surfaces of very low intensity, as in galvanic batteries even in their state of highest tension, they are imperfect conductors. Even water, when quite pure, transmits the electricity of a galvanic apparatus so imperfectly, that a very powerful battery occasions a slow disengagement of gas, when its opposite poles communicate through distilled water. Its conducting power is greatly improved by adding a little saline matter, such as the sulphate of soda or potassa; and the same battery which decomposed water feebly before the addition of the salt, will then cause a free disengagement of gas.

III. The power of lightning in destroying and reversing the poles of a magnet, and of communicating magnetic properties to pieces of iron which did not previously possess them, was noticed at an early period of the science of electricity, and led to the supposition that similar effects may be produced by the common electrical or galvanic apparatus. Attempts were accordingly made to communicate the magnetic virtue by means of electricity or galvanism; but no results of importance were obtained till the winter of 1819, when Professor Oersted of Copenhagen made his famous discovery, which forms the basis of a new branch of science called *electro-magnetism.* (Annals of Philosophy, xvi. 273.)

The fact observed by Professor Oersted was, that an electric current, such as is supposed to pass from the positive to the negative pole of a Voltaic battery along a wire which connects them, causes a magnetic needle placed near it to deviate from its natural position, and assume a new one, the direction of which depends upon the relative position of the needle and the wire. On placing the wire above the magnet and parallel to it, the pole next the negative end of the battery always moves westward, and when the wire is placed under

the needle, the same pole goes towards the east. If the wire is on the same horizontal plane with the needle, no declination whatever takes place; but the magnet shows a disposition to move in a vertical direction, the pole next the negative side of the battery being depressed when the wire is to the west of it, and elevated when it is placed on the east side.

The extent of the declination occasioned by a battery depends upon its power, and the distance of the connecting wire from the needle. If the apparatus is powerful, and the distance small, the declination will amount to an angle of 45°. But this deviation does not give an exact idea of the real effect which may be produced by galvanism; for the motion of the magnetic needle is counteracted by the magnetism of the earth. When the influence of this power is destroyed by means of another magnet, the needle will place itself directly across the connecting wire; so that the real tendency of a magnet is to stand at right angles to an electric current.

The communicating wire is also capable of attracting and repelling the poles of a magnet. If, when the magnet and connecting wire are at right angles to each other, the latter passing across the centre of the former, the wire be moved along the needle towards either extremity, attraction will take place between the wire and the adjacent pole: and this will occur though the same point of the wire should be presented in succession to both of the poles. Again, if the position of the poles of the needle be reversed, they will be repelled by the same point of the wire which had previously attracted them*.

This discovery was no sooner announced, than the experiments were repeated and varied by philosophers in all parts of Europe, and, as was to be expected, new facts were speedily brought to light. Among the most successful labourers in this field, MM. Ampère, Arago, and Biot of Paris, and Sir H. Davy and Mr Faraday in this country, deserve to be particularly mentioned.

M. Ampère observed that the Voltaic apparatus itself acts on a magnetic needle placed upon or near it in the same manner as the wire which unites its two extremities. But the declination was found to occur only when the opposite ends of the battery are in communication, and to cease entirely as soon as the circuit is interrupted,—a difference which was supposed to arise from the passage of an uninterrupted electric current through the apparatus, as along the connecting wire, taking place in the first case, and not in the second. M. Ampère therefore proposed the magnetic needle as an instrument for discovering the existence and direction of an electric current, (or currents according to the theory of the two electricities), as well as for pointing out the proper state and fitness of a galvanic apparatus for electro-magnetic experiments in general. When the needle is employed with this intention it is called a *galvanometer*.

M. Ampère soon after discovered that a power of attraction and repulsion may be communicated by an electric current alone, without the use of a magnet. Two wires of copper, brass, or any other metal, placed parallel to one another, and suspended so as to move freely, were connected with the opposite poles of a galvanic apparatus. If the electric current passed along both wires in the same direction, they attracted one another; if in an opposite direction, they repelled

* The clearest statement of this fact which I have seen is in the historical sketch of Electro-magnetism by Mr Faraday. (Annals of Philosophy. New Series, vol. ii.)

each other. The result of this experiment gave rise to the supposition that the magnetic property is actually communicated to the wires by the electric current; and this supposition was confirmed by M. Arago, who found that iron filings are attracted by a wire placed in the Voltaic circuit, and that they all fall off when the communication between the poles is interrupted. This fact was also discovered about the same time by Sir H. Davy, who has minutely described his experiments in a paper in the Philosophical Transactions for 1821.

The communication of temporary magnetic properties to the common metals naturally led to an attempt to magnetize steel and iron permanently by the same agent. The experiment was made by M. Arago and Sir H. Davy about the same time, and both were successful. Sir H. Davy attached steel needles to the connecting wire, some parallel to it, and others transversely. The former merely acted as a part of the circuit; they did not possess poles, and lost their power of attracting iron filings as soon as the electric current ceased to circulate through them. But the latter acquired a north and south pole, and preserved the property after separation from the wire. M. Arago at first operated in a similar manner; but, at the suggestion of M. Ampère, he made the connecting wire into the form of a spiral or helix, and placed the needle to be magnetized in its centre. By this arrangement the maximum effect was obtained in a shorter time than by any other method. Sir H. Davy also rendered a needle magnetic by placing it across a wire, along which a charge from a common Leyden battery was transmitted. This series of experiments was completed by M. Ampère's discovery, that a connecting wire, suspended so as to have perfect freedom of motion, is influenced by the magnetic attraction of the earth.

For the next fact of importance, science is indebted to the researches of Mr Faraday. He ascertained that the action of the connecting wire on the direction of a magnet, is not owing to any attraction or repulsion exerted between them, but to a tendency they have to revolve round each other. He contrived an apparatus, (Quarterly Journal, vol. xii.), by means of which either pole of a magnet was made to revolve round the wire as a fixed point; and then, by fixing the wire, and giving free motion to the magnet, both poles of the latter were made to revolve in succession round the former.

He was also successful in causing the wire to revolve by the influence of the magnetism of the earth.

These magnetic properties of the Voltaic apparatus, which form the basis of electro-magnetism, were discovered soon after the original experiments of Oersted were made known to the public. Other facts of interest have since been observed, and some ingenious general views have been proposed to account for all the phenomena: but as a full discussion of electro-magnetism would lead into details too minute for an elementary treatise, I must refer the reader, who may wish for more ample information, to works written professedly on the subject. In addition to the papers already alluded to, the "Recueil d'Observations Electro-dynamiques" by M. Ampère, and the second edition of Mr Barlow's Essay on Magnetic Attractions, will be consulted with much advantage.

## *On the Theory of the Pile.*

There are three principal theories concerning the action of the Voltaic pile or battery. The first originated with Volta, who conceiv-

ed that the electricity is set in motion, and the supply kept up, solely by the contact of the metals. He regarded the interposed solutions merely as conductors, by means of which the electricity, developed by each pair of plates, is conveyed from one part of the apparatus to the other.

Volta attached little importance to the chemical action going on between the plates of the pile, and the fluid by which it is excited: he considered these changes as contributing nothing to the general result, and accordingly left them wholly out of view in the formation of his theory. But the repetition and extension of his experiments by the English chemists soon demonstrated that Volta had committed a material error in overlooking the chemical phenomena which occur between the plates of the pile and the liquid contained in its cells. For it was observed that no sensible effects are produced by a combination formed of substances that have no chemical action on each other; that the action of the pile is always accompanied by the oxidation of the zinc; and that the energy of the pile in producing chemical decomposition, a subject which at that time excited intense interest, is in some proportion to the activity of the chemical action within the apparatus itself. Observations of this nature induced Dr Wollaston to conclude, that the process begins with the oxidation of the zinc—that the oxidation is the primary cause of the development of electricity; and he published several ingenious experiments in the Philosophical Transactions for 1801 in support of his opinion.—This constitutes the second or chemical theory of the pile, and is in direct opposition to that proposed by Volta.

Plausible as appeared the chemical theory of the pile at the time it was first announced, more extensive observation has proved it to be inconsistent with some of the phenomena of galvanism. It must now be admitted, I apprehend, as established, that the mere contact of substances, without any chemical change whatever, is adequate to the excitement of electricity; and that the energy of the pile, in respect to its electrical properties, is not in proportion to the chemical action produced by the liquid with which it is charged. It appears, also, that in the mere act of chemical union, no electrical excitement is manifested. M. Becquerel indeed has stated the contrary, but the fact is denied by Sir H. Davy. It is found, likewise, by the late researches of the same chemist, that galvanism, to an extent capable of decomposing water, may be excited by a galvanic combination, in which no chemical action whatever occurs.

The third theory of the pile is intermediate between the two others, and was proposed by Sir H. Davy. He inferred from numerous experiments, that there is no reason to question the fact originally stated by Volta, that the electric equilibrium is disturbed by the contact of different substances without any chemical action taking place between them. He acknowledged, however, with Dr Wollaston, that the chemical changes contribute to the general result; and maintained that, though not the primary cause of the phenomenon, they are so far essential, that without such changes the galvanic excitement can neither be considerable in degree, nor of long duration. In his opinion the action is commenced by the contact of the metals, and kept up by the chemical phenomena.

The mode in which Sir H. Davy conceives the chemical changes act, is by restoring the electric equilibrium whenever it is disturbed. By the contact of the zinc and copper plates, the former is rendered positive throughout the whole series, and the latter negative; and by

means of the conducting fluid with which the cells are filled, the electricity accumulates on one side of the battery, and the other becomes as strongly negative. But the quantity of electricity, thus excited, would not be sufficient, as is maintained, for causing energetic action. For this effect, the electric equilibrium of each pair of plates must be restored as soon as it is disturbed, in order that they may be able to furnish an additional supply of electricity. The chemical substances of the solution are supposed to effect that object in the following manner. The negative ingredients of the liquid, such as oxygen and the acids, pass over to the zinc; while the hydrogen and the alkalies, which are positive, go to the copper; in consequence of which, both the metals are for the moment restored to their natural condition. But as the contact between them continues, the equilibrium is no sooner restored than it is again disturbed; and when, by a continuance of the chemical changes, the zinc and copper recover their natural state, electricity is again developed by a continuance of the same condition by which it was excited in the first instance. In this way Sir H. Davy explains why chemical action, though not essential to the first development of electricity, is necessary for enabling the Voltaic appparatus to act with energy.

# PART II.

## PRELIMINARY REMARKS.

IN teaching a science, the details of which are numerous and complicated, it would be injudicious to follow the order of discovery and proceed from the individual facts to the conclusions which have been deduced from them. An opposite course is indispensable. It is necessary to discuss the general principles in the first instance, in order to aid the beginner in remembering the insulated facts, and comprehending the explanations connected with them.

This necessity is in no case more sensibly felt than in the study of chemistry, and for this reason I shall commence the second part of the work by explaining the leading doctrines of the science. One inconvenience, indeed, does certainly arise from this method. It is often necessary, by way of illustration, to refer to facts of which the beginner is ignorant; and therefore on some occasions more knowledge will be required for understanding a subject fully, than the reader may have at his command. But these instances will, it is hoped, be rarely met with; and when they do occur, the reader is advised to quit the point of difficulty, and return to the study of it, when he shall have acquired more extensive knowledge of the details.

To the chemical history of each substance its chief physical characters will be added. A knowledge of these properties is not only advantageous in assisting the chemist to distinguish one body from another, but in many instances is put to uses still more important. The specific gravity in particular is of great consequence; and as this expression will hereafter be used in almost every page, it will be proper, before proceeding further, to explain its meaning. Equal bulks of different substances, as a cubic inch of gold, silver, tin, and water, differ more or less in weight: their densities are different; or in other words, they contain different quantities of ponderable matter in the same space. The tin will weigh eight times more than the water, the silver about ten times and a half, and the gold upwards of nineteen times more than that fluid. The density of all solids and liquids may be determined in the same manner; and if they are compared with an equal bulk of water as a standard of comparison, a series of numbers will be obtained, which will show the comparative density or specific gravity, as it is called, of all of them.

The process for determining specific gravities is, therefore, sufficiently simple. It consists in weighing a body carefully, and then determining the weight of an equal bulk of water, the latter being regarded as unity. If, for example, a portion of water weighs nine grains, and the same bulk of another body 20 grains, its specific gra-

vity is determined by the formula, as 9 : 20 : : 1 (the specific gravity of water) to the fourth proportional 2.2222: so that the specific gravity of any substance is found by dividing its weight by the weight of an equal volume of water. It is easy to discover the weight of equal bulks of water and any other liquid by filling a small bottle of known weight with each successively, and weighing them*. The method of obtaining the necessary data in case of a solid is somewhat different. The body is first weighed in air, is next suspended in water by means of a hair attached to the scale of the balance, and is then weighed again. The difference between the two weights gives the weight of a quantity of water equal to the bulk of the solid. This rule is founded on the hydrostatic law, that a solid body, fully immersed in any liquid, weighs precisely so much less than it does in air as is equal to the weight of the liquid which it displaces; and it is obvious that the liquid so displaced is exactly of the same dimensions as the solid. Another method is by the use of the bottle recommended for taking the specific gravity of liquids. After weighing the bottle filled with water, a known weight of the solid is put into it, which of course displaces a quantity of water precisely equal to its own volume. The exact weight of the displaced water is found by weighing the bottle again, after having wiped its outer surface with a dry cloth.

The determination of the specific gravity of gaseous substances is an operation of much greater delicacy. From the extreme lightness of gases, it would be inconvenient to compare them with an equal bulk of water, and therefore atmospheric air is taken as the standard of comparison. The first step of the process is to ascertain the weight of a given volume of air. This is done by weighing a very light glass flask, furnished with a good stopcock, while full of air; and then weighing it a second time, after the air has been withdrawn by means of the air-pump. The difference between the two weights gives the information required. According to the experiments of Sir George Shuckburgh, 100 cubic inches of pure and dry atmospheric air, at the temperature of 60° F. and when the barometer stands at 30 inches, weigh precisely 30.5 grains†. By a similar method the weight of any other gas may be determined, and its specific gravity be inferred accordingly. Thus, suppose 100 cubic inches of oxygen are found to weigh 33.888 grains, its specific gravity will be thus deduced; as 30.5 : 33.888 : : 1 (the sp. gr. of air) : 1.1111, the specific gravity of oxygen.

There are four circumstances to which particular attention must be paid in taking the specific gravity of gases:—

1. The gas should be perfectly pure, otherwise the result cannot be accurate.

2. Due regard must be had to its hygrometric condition. If it is

* Bottles are prepared for this purpose by the Philosophical Instrument-makers.

† Dr Prout is at present occupied with the investigation of this important subject; and though he has not yet brought his researches to a conclusion, he permits me to state that 100 cubic inches of pure atmospheric air, at 60° F. and 30 inches of the barometer, weigh at least 31 grains. The estimate of 30.5 grains, deduced from the observations of Shuckburgh, is, therefore, inaccurate.—*Addendum by Dr Turner.*

saturated with moisture, the necessary correction may be made for that circumstance by the formula page 63; or it may be dried by the use of substances which have a powerful attraction for moisture, such as the chloride of calcium, quicklime, or fused potassa.

3. As the bulk of gaseous substances, owing to their elasticity and compressibility, is dependent on the pressure to which they are exposed, no two observations admit of comparison, unless made under the same elevation of the barometer. It is always understood, in taking the specific gravity of a gas, that the barometer must stand at thirty inches, by which means the operator is certain that each gas is subject to equal degrees of compression. An elevation of thirty inches is, therefore, called the standard height; and if the mercurial column be not of that length at the time of performing the experiment, the error arising from this cause must be corrected by calculation. It has been established by careful experiment that the bulk of gases is inversely as the pressure. Thus, 100 measures of air under the pressure of a thirty inch column of mercury, will dilate to 200 measures, if the pressure be diminished by one half; and will be compressed to 50 measures, when the pressure is double or equal to a mercurial column of sixty inches. The correction for the effect of pressure may therefore be made by the rule of three, as will appear by an example. If a certain portion of gas occupy the space of 100 measures at twenty-nine inches of the barometer, its bulk at thirty inches may be obtained by the following proportion; as

$$30 : 29 : : 100 : 96.66.$$

4. For a similar reason the temperature should always be the same. The standard or mean temperature is 60° F. and if the gas be admitted into the weighing flask when the thermometer is above or below that point, the formula of page 35 should be employed for making the necessary correction.

Chemistry is indebted for its nomenclature to the labours of four celebrated chemists, Lavoisier, Berthollet, Guyton-Morveau, and Fourcroy. The principles which guided them in its construction are exceedingly simple and ingenious. The known elementary substances and the more familiar compound ones were allowed to retain the appellations which general usage had assigned to them. The newly discovered elements were named from some striking property. Thus, as it was supposed that acidity was always owing to the presence of the vital air discovered by Priestley and Scheele, they gave it the name of *oxygen*, derived from two Greek words signifying generator of acid; and they called inflammable air, *hydrogen*, from the circumstance of its entering into the composition of water.

Compounds with which oxygen forms a part were called *acids* or *oxides*, according as they do or do not possess acidity. An oxide of iron or copper signifies a combination of those metals with oxygen, which has no acid properties. The name of an acid was derived from the substance acidified by the oxygen, to which was added the termination in *ic*. Thus, sulphur*ic* and carbon*ic* acids signify acid compounds of sulphur and carbon with oxygen gas. If sulphur or any other body should form two acids, that which contains the least quantity of oxygen is made to terminate in *ous*, as sulphur*ous* acid. The termination in *uret* was intended to denote combinations of the simple non-metallic substances, either with one another, with a metal, or with a metallic oxide. Sulph*uret* and carb*uret* of iron, for example, signify compounds of sulphur and carbon with iron. The different

oxides or sulphurets of the same substance were distinguished from one another by some epithet, which was commonly derived from the colour of the compound, such as the black and red oxides of iron, the black and red sulphurets of mercury. Though this practice is still continued occasionally, it is now more customary to distinguish degrees of oxidation by the use of derivatives from the Greek. *Pro*toxide signifies the first degree of oxidation, *deut*oxide the second, *trit*oxide the third, and *per*oxide the highest. The sulphurets, carburets, &c. of the same substance are designated in a similar way. The combination of acids with alkalies, earths, or metallic oxides, were termed *salts*, the names of which were so contrived as to indicate the substances contained in them. If the acidified substance contains a maximum of oxygen, the name of the salt terminates in *ate*; if a minimum, the termination in *ite* is employed. Thus, the sulph*ate*, phosph*ate*, and arseni*ate* of potassa, are salts of sulphur*ic*, phosphor*ic*, and arsen*ic* acids; while the terms sulph*ite*, phosph*ite*, and arsen*ite* of potassa, denote combinations of that alkali with the sulphur*ous*, phosphor*ous*, and arseni*ous* acids.

The advantage of a nomenclature which disposes the different parts of a science in so systematic an order, and gives such powerful assistance to the memory, is incalculable. The principle has been acknowledged in all countries where chemical science is cultivated, and its minutest details have been adopted in Britain. It must be admitted, indeed, that in some respects the nomenclature is defective. The erroneous idea of oxygen being the general acidifying principle, has exercised an injurious influence over the whole structure. It would have been convenient also to have had a different name for hydrogen. But it is now too late to attempt a change; for the confusion attending such an innovation would more than counterbalance its advantages. The original nomenclature has therefore been preserved, and such additions made to it as the progress of the science rendered necessary. The most essential improvement has been suggested by the discovery of the laws of chemical combination. The different salts formed of the same constituents were formerly divided into *neutral*, *super*, and *sub*-salts. They were called neutral if the acid and alkali are in the proportion for neutralizing one another; super-salts if the acid prevails; and sub-salts, if the alkali is in excess. The name is now regulated by the atomic constitution of the salt. If it be a compound of one equivalent of the acid to one equivalent of the alkali, the generic name of the salt is employed without any other addition; but if two or more equivalents of the acid be attached to one of the base, or two or more equivalents of the base to one of the acid, a numeral is prefixed so as to indicate its composition. The two salts of sulphuric acid and potassa are called sulphate and *bi*-sulphate; the first containing one equivalent of the acid to one equivalent of the alkali, and the second salt, two of the former to one of the latter. The three salts of oxalic acid and potassa are termed the oxalate, *bin*oxalate, and *quadro*xalate of potassa; because one equivalent of the alkali is united with one equivalent of acid in the first, with two in the second, and with four in the third salt. As the numerals which denote the equivalents of the acid in a super-salt are derived from the Latin language, Dr Thomson proposes to employ the Greek numerals, *dis*, *tris*, *tetrakis*, to signify the equivalents of alkali in a sub-salt.

This method is in the true spirit of the original framers of our nomenclature. Chemists have already begun to apply the same principle to

other compounds besides salts; and there can be no doubt that it will be applied universally whenever our knowledge shall be in a state to admit of its introduction.

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## SECTION I.

### *AFFINITY.*

All chemical phenomena are owing to Affinity or chemical attraction. It is the basis on which the science of chemistry is founded. It is, as it were, the instrument which the chemist employs in all his operations, and hence forms the first and leading object of his study.

Affinity is exerted between the minutest particles of different kinds of matter, causing them to combine so as to form new bodies endowed with new properties. It acts only at insensible distances; in other words, apparent contact, or the closest proximity, is necessary to its action. Every thing which prevents such contiguity is an obstacle to combination, and any force which increases the distance between particles already combined, tends to separate them permanently from each other. In the first case, they do not come within the sphere of their mutual attraction; in the second, they are removed out of it. It follows, therefore, that though affinity is regarded as a specific power, distinct from the other forces which act on matter, its action may be promoted, modified, or counteracted by several circumstances; and consequently, in studying the phenomena produced by affinity, it is necessary to inquire into the conditions that influence its operation.

The most simple instance of the exercise of chemical attraction is afforded by the mixture of two substances with one another. Water and sulphuric acid, or water and alcohol, combine readily. On the contrary, water shows little disposition to unite with sulphuric ether, and still less with oil; for however intimately their particles may be mixed together, they are no sooner left at rest than the ether separates almost entirely from the water, and a total separation takes place between that fluid and the oil. Sugar dissolves very sparingly in alcohol, but to any extent in water; while camphor is dissolved in very small quantity by water, and abundantly by alcohol. It appears, from these examples, that chemical attraction is exerted between different bodies with different degrees of force. There is sometimes no proof of its existence at all; between some substances it acts very feebly, and between others with great energy.

Simple combination of two particles is a common occurrence. The solution of salts in water, the combustion of phosphorus in oxygen gas, and the neutralization of a pure alkali by an acid, are instances of the kind. The phenomena however are often more complex. It frequently happens that the formation of a new compound is attended by the destruction of an existing one. The only condition necessary for this effect, is the presence of some third body which has a greater affinity for one of the elements of a compound than they have for each other. Thus, oil has an affinity for the volatile alkali, ammonia, and will unite with it, forming a soapy substance called a liniment. But the ammonia has a still greater attraction for sulphuric acid; and hence if this acid be added to the liniment, the alkali will quit the oil, and

unite by preference with the acid. If a solution of camphor in alcohol be poured into water, the camphor will be set free, because the alcohol combines with the water. Sulphuric acid, in like manner, separates baryta from muriatic acid. Combination and decomposition occur in each of these cases;—combination of sulphuric acid with ammonia, of water with alcohol, and of baryta with sulphuric acid;—decomposition of the compounds formed of oil and ammonia, of alcohol and camphor, and of muriatic acid and baryta. These are examples of what Bergmann called *single elective affinity;*—elective, because a substance manifests, as it were, a choice for one of two others, uniting with it by preference, and to the exclusion of the other. Many of the decompositions that occur in chemistry are instances of single elective affinity.

The order in which these decompositions take place has been expressed in tables; of which the following, drawn up by Geoffroy, is an example:—

*Sulphuric Acid.*

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Baryta,
Strontia,
Potassa,
Soda,
Lime,
Ammonia,
Magnesia.

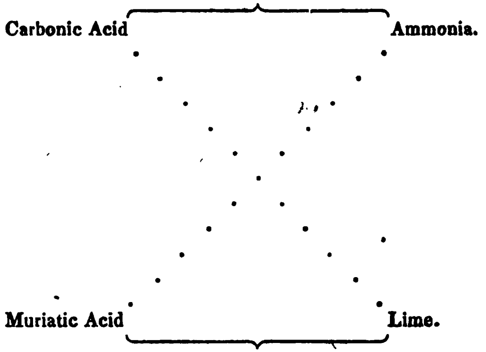
This table signifies, first, that sulphuric acid has an affinity for the substances placed below the horizontal line, and may unite separately with each; and, secondly, that the basis of the salts so formed will be separated from the acid by adding any of the alkalies or earths which stand above it in the column. Thus ammonia will separate magnesia, lime ammonia, and potassa lime; but none can withdraw baryta from sulphuric acid, nor can ammonia or magnesia decompose the sulphate of lime, though strontia or baryta will do so. Bergmann conceived that these decompositions are solely determined by chemical attraction, and that consequently the order of decomposition represents the comparative forces of affinity; and this view, from the simple and natural explanation it affords of the phenomenon, was for a time very generally adopted. But Bergmann was in error. It does not necessarily follow, because lime separates ammonia from sulphuric acid, that the lime has a greater attraction for the acid than the volatile alkali. Other causes are in operation which modify the action of affinity to such a degree, that it is impossible to discover how much of the effect is owing to that power. It is conceivable that ammonia may in reality have a stronger attraction for sulphuric acid than lime, and yet the latter, from the great influence of disturbing causes, may succeed in decomposing the sulphate of ammonia.

The justness of the foregoing remark will be made obvious by the following example.—When a stream of hydrogen gas is passed over the oxide of iron heated to redness, the oxide is reduced to the metallic state and water is generated. On the contrary, when watery vapour is brought into contact with red-hot metallic iron, the oxygen of the water quits the hydrogen and combines with the iron. It follows from the result of the first experiment, according to Bergmann, that hydrogen has a stronger attraction than iron for oxygen; and from that of the second, that iron has a greater affinity for oxygen than hy-

drogen. But these inferences are incompatible with one another. The affinity of oxygen for the two elements hydrogen and iron, must either be equal or unequal. If equal, the result of both experiments was determined by modifying circumstances; since neither of these substances ought on this supposition to take oxygen from the other. But if the forces are unequal, the decomposition in one of the experiments must have been determined by extraneous causes in direct opposition to the tendency of affinity.

To Berthollet is due the honour of pointing out the fallacy of Bergmann's opinion. He was the first to show that the relative forces of chemical attraction cannot always be determined by observing the order in which substances separate each other when in combination, and that the tables of Geoffroy are merely tables of decomposition, not of affinity. He likewise traced all the various circumstances that modify the action of affinity, and gave a consistent explanation of the mode in which they operate. Berthollet went even a step further. He denied the existence of elective affinity as an invariable force, capable of effecting the perfect separation of one body from another; he maintained that all the instances of complete decomposition attributed to elective affinity are in reality determined by one or more of the collateral circumstances that influence its operation. But here this acute philosopher has surely gone too far. Bergmann is admitted to have erred in supposing the result of chemical action to be in every case owing to elective affinity; but Berthollet certainly ran into the opposite extreme in declaring that the effects formerly ascribed to that power are never produced by it. That chemical attraction is exerted between bodies with different degrees of energy is, I conceive, indisputable. Water has a much greater affinity for muriatic acid and ammoniacal gases than for carbonic acid and sulphuretted hydrogen, and for these than for oxygen and hydrogen. The attraction of lead for oxygen is greater than that of silver for the same substance. The disposition of gold and silver to combine with mercury, is greater than the attraction of platinum and iron for that fluid. As these differences cannot be accounted for by the operation of any modifying causes, we must admit a difference in the force of affinity in producing combination. It is equally clear that in some instances the separation of bodies from one another can only be explained on the same principle. No one, I conceive, will contend that the decomposition of hydriodic acid by chlorine, or of sulphuretted hydrogen by iodine, is determined by the concurrence of any modifying circumstances.

Affinity is the cause of still more complicated changes than those which have been just considered. In a case of single elective affinity three substances only are present, and two affinities are in play. But it frequently happens that two compounds are mixed together, and four different affinities brought into action. The changes that may or do occur under these circumstances are most conveniently studied by aid of a diagram,—a method which was first employed, I believe, by Dr Black, and has since been generally practised. Thus in mixing together a solution of the carbonate of ammonia and muriate of lime, their mutual action may be represented in the following manner:




Each of the acids has an attraction for both bases, and hence it is possible either that the two salts should continue as they are, or that an interchange of principles should ensue, giving rise to two new compounds,—the carbonate of lime and muriate of ammonia. According to the views of Bergmann the result is solely dependent on the comparative strength of affinities. If the affinity of carbonic acid for ammonia, and of muriatic acid for lime, exceed that of carbonic acid for lime, added to that of muriatic acid for ammonia, then will the two salts experience no change whatever; but if the latter affinities preponderate, then, as does actually happen in the present example, both the original salts will be decomposed, and two new ones generated. Two decompositions and two combinations take place, being an instance of what is called *double elective affinity*. Mr Kirwan applied the terms *quiescent* and *divellent* to denote the tendency of the opposing affinities, the action of the former being to prevent a change, the latter to produce it.

The doctrine of double elective affinity was assailed by Berthollet on the same ground and with the same success as in the case of single elective attraction. He succeeded in proving that the effect cannot always be ascribed to the sole influence of affinity. For, to take the example already adduced, if carbonate of ammonia decompose muriate of lime by the mere force of a superior attraction, it is manifest that carbonate of lime ought never to decompose muriate of ammonia. But if these two salts are mixed in a dry state and exposed to heat, double decomposition does take place, carbonate of ammonia and muriate of lime being formed; and therefore if the change in the first example was produced by chemical attraction alone, that in the second must have occurred in direct opposition to that power. It does not follow, however, because the result is sometimes determined by modifying conditions, that it must always be so. I apprehend that the decomposition of the solid cyanuret of mercury by sulphuretted hydrogen gas, which takes place even at a low temperature, cannot be ascribed to any other cause than a preponderance of the divellent over the quiescent affinities.

## *On the Changes that accompany Chemical Action.*

The leading circumstance that characterises chemical action is the loss of properties experienced by the combining substances, and the acquisition of new ones by the product of their combination. The change of property is sometimes inconsiderable. In a solution of sugar or salt in water, and in mixtures of water with alcohol or sulphuric acid, the compound retains so much of the character of its constituents, that there is no difficulty in recognising their presence. But more generally the properties of one or both of the combining bodies disappear entirely. No ingenuity could guess, *a priori*, that water is a compound body, much less that it is composed of two gases, oxygen and hydrogen, neither of which, when uncombined, has ever been compressed into a liquid. Hydrogen is one of the most inflammable substances in nature, and yet water cannot be set on fire; oxygen, on the contrary, enables bodies to burn with great brilliancy, and yet water extinguishes combustion. The alkalies and earths were regarded as simple till Sir H. Davy proved them to be compound, and certainly they evince no sign whatever of containing oxygen and a metal. Numerous examples of a similar kind are afforded by the action of acids and alkalies on one another. Sulphuric acid and potassa, for example, are highly caustic. The former is intensely sour, reddens the blue colour of vegetables, and has a strong affinity for alkaline substances; the latter has a pungent taste, converts the blue colour of vegetables to green, and combines readily with acids. On adding these principles cautiously to one another, a compound result called a *neutral salt*, which does not in any way affect the colouring matter of plants, and in which the other distinguishing features of the acid and alkali can no longer be perceived. They appear to have destroyed the properties of each other, and are hence said to *neutralize* one another.

The other phenomena that acccompany chemical action are changes of density, temperature, form, and colour.

1. It is observed that two bodies rarely occupy the same space after combination as they did separately. In general their bulk is diminished, so that the specific gravity of the new body is greater than the mean of its components. Thus a mixture of 100 measures of water and an equal quantity of sulphuric acid do not occupy the space of 200 measures, but considerably less. A similar contraction frequently attends the combination of solids. Gases often experience a remarkable condensation when they unite. The elements of olefiant gas, for instance, would expand to four times the bulk of that compound, if they were suddenly to become free, and assume the gaseous form. But the rule is not without exception. The reverse happens in some metallic compounds; and there are examples of combination between gases without any change of bulk.

2. A change of temperature generally accompanies chemical action. Caloric is evolved either when there is a diminution in the bulk of the combining substances without a change of form, or when a gas is condensed into a liquid, or when a liquid becomes solid. The heat caused by mixing sulphuric acid with water is an instance of the former; and the common process of slacking lime, during which water loses its liquid form in combining with that earth, is an example of the second. The rise of temperature in these cases is obviously referable to a diminution in the capacity of the new compound for

caloric; but an intense degree of heat sometimes accompanies chemical action under circumstances in which an explanation founded on a change of specific caloric is quite inadmissible. At present it is enough to have stated the fact; the theory of it will be discussed under the subject of combustion. The production of cold seldom or never takes place during combination, except when the specific caloric is suddenly increased by the conversion of a solid into a liquid, or a liquid into a gas. All the frigorific mixtures act in this way.

3. The changes of form that attend chemical action are exceedingly various. The combination of gases may give rise to a liquid or a solid; solids sometimes become liquid, or liquids solid. Several familiar chemical phenomena, such as explosions, effervescence, and precipitations, are owing to these changes. The sudden evolution of a large quantity of gaseous matter occasions an explosion, as when gunpowder detonates. The slower disengagement of gas causes effervescence, as occurs when marble is put into muriatic acid. A precipitate is owing to the formation of a new body which happens to be insoluble in the liquid in which its elements were dissolved.

4. The colour of a compound is frequently quite different from that of the substances by which it is formed. There does not appear to be any uniform relation between the colour of a body and that of its elements; so that it is not possible to anticipate the colour of any particular compound by knowing the principles which enter into its composition. Iodine, whose vapour is of a violet hue, forms a beautiful red compound with mercury, and a yellow one with lead. The brown oxide of copper generally gives rise to green and blue coloured salts: while the salts of the oxide of lead, which is itself yellow, are for the most part colourless. The colour of precipitates is a very important study, as it often enables the chemist to distinguish bodies from one another when in solution.

## *On the Circumstances that modify and influence the Operation of Affinity.*

Of the conditions which are capable of promoting or counteracting the tendency of chemical attraction, the following are the most important;—cohesion, elasticity, quantity of matter, and gravity. To these may be added the agency of the imponderables.

### *Cohesion.*

The first obvious effect of cohesion is to oppose affinity, by impeding or preventing that mutual penetration and close proximity of the particles of different bodies, which is essential to the successful exercise of their attraction. For this reason bodies seldom act chemically in their solid state; their molecules do not come within the sphere of attraction, and therefore combination cannot take place, although their affinity may in fact be considerable. Liquidity, on the contrary, favours chemical action; it permits the closest possible approximation, while the cohesive power is comparatively so trifling as to oppose no appreciable barrier to affinity.

Cohesion may be diminished in two ways, by mechanical division, or by the application of heat. The former is useful by increasing the extent of surface: but it is not of itself in general sufficient, because the particles, however minute, still retain that degree of cohesion

which constitutes solidity. Caloric acts with greater effect, and never fails in promoting combination, whenever the cohesive power is a barrier to it. Its intensity should always be so regulated as to produce liquefaction. It is often enough to liquefy one of the substances, as is proved by the facility with which water dissolves many salts and other solid bodies. But it is easy to perceive that the cohesive power is still in operation: for a solid is commonly dissolved in greater quantity when its cohesion is diminished by caloric. The reduction of both substances to the liquid state is the best method for ensuring chemical action. The slight degree of cohesion possessed by liquids does not appear to cause any impediment to combination; for they commonly act as energetically on each other at low temperatures, or at a temperature just sufficient to cause perfect liquefaction, as when their cohesive power is still further diminished by caloric. It seems fair to infer, therefore, that very little, if any, affinity exists between two bodies, which do not combine when they are intimately mixed in a liquid state.

The phenomena of crystallization are owing to the ascendency of cohesion over affinity. When a large quantity of salt has been dissolved in water by the aid of heat, part of the saline matter generally separates as the solution cools, because the cohesive power of the salt then becomes comparatively too powerful for chemical attraction. Its particles begin to cohere together, and are deposited in crystals, the process of crystallization continuing till it is arrested by the affinity of the liquid. A similar change happens when a solution made in the cold is gradually evaporated. The cohesion of the saline particles is no longer counteracted by the affinity of the liquid, and the salt therefore assumes the solid form.

Cohesion plays a still more important part. It sometimes determines the result of chemical action, probably even in opposition to affinity. Thus, on mixing together a solution of two acids and one alkali, of which two salts may be formed, one soluble and the other insoluble, the alkali will unite with that acid, with which it forms the insoluble compound, to the total exclusion of the other. This is one of the modifying circumstances employed by Berthollet to account for the phenomena of single elective attraction, and it certainly is applicable to many of the instances to be found in the tables of affinity. When, for example, muriatic acid, sulphuric acid, and baryta, are mixed together, the sulphate of baryta is formed in consequence of its insolubility. Lime, which yields an insoluble salt with carbonic acid, separates that acid from ammonia, potassa, and soda, with all of which it makes soluble compounds.

A similar explanation may be given of many cases of double elective attraction. On mixing together in solution four substances, A, B, C, D, of which it is possible to form four compounds, AB and CD, or AC and BD, that compound will certainly be produced which happens to be insoluble. Thus sulphuric acid, soda, muriatic acid, and baryta, may give rise either to sulphate of soda and muriate of baryta, or sulphate of baryta and muriate of soda; but the first two salts cannot exist together in the same liquid, because the insoluble sulphate of baryta is instantly generated, and its formation necessarily causes the muriatic acid to combine with the soda. In like manner, muriate of lime is decomposed by carbonate of ammonia, in consequence of the insolubility of carbonate of lime.

To comprehend the manner in which cohesion acts in these instances, it is necessary to consider what takes place when in the same liquid

two or more compounds are brought together, which do not give rise to an insoluble substance. Thus on mixing solutions of sulphate of potassa and muriate of soda, no precipitate ensues; because the salts capable of being formed by double decomposition, sulphate of soda and muriate of potassa, are likewise soluble. In this case it is possible either that each acid may be confined to one base, so as to constitute two neutral salts; or that each acid may be divided between both bases, yielding four neutral salts. It is difficult to decide this point in an unequivocal manner; but judging from many chemical phenomena, there can, I apprehend, be no doubt that the arrangement last mentioned is the most frequent, and is probably universal whenever the relative forces of affinity are not very unequal. When two acids and two bases meet together in neutralizing proportion, it may therefore be inferred, that each acid unites with both the bases in a manner regulated by their respective forces of affinity, and that four salts are contained in solution. In like manner the presence of three acids and three bases will give rise to nine salts; and when four of each are present, sixteen salts will be produced. This view affords the most plausible theory of the constitution of mineral waters, and of the products which they yield by evaporation.

The influence of insolubility in determining the result of chemical action may be readily explained on this principle. If muriatic acid, sulphuric acid, and baryta are mixed together in solution, the base may be conceived to be at first divided between the two acids, and the muriate and sulphate of baryta to be generated. The latter being insoluble is instantly removed beyond the influence of the muriatic acid, so that for an instant muriate of baryta and free sulphuric acid remain in the liquid; but as the base left in solution is again divided between the two acids, a fresh quantity of the insoluble sulphate is generated; and this process of partition continues, until either the baryta or the sulphuric acid is withdrawn from the solution. Similar changes ensue when muriate of baryta and sulphate of soda are mixed.

The separation of salts by crystallization from mineral waters or other saline mixtures is explicable by a similar mode of reasoning. Thus on mixing muriate of potassa and sulphate of soda, four salts according to this view are generated, namely, the sulphates of soda and potassa, and the muriates of those bases; and if the solution be allowed to evaporate gradually, a point at length arrives when the least soluble of these salts, the sulphate of potassa, will be disposed to crystallize. As soon as some of its crystals are deposited, and thus withdrawn from the influence of the other salts, the constituents of these undergo a new arrangement, whereby an additional quantity of the sulphate of potassa is generated; and this process continues until the greater part of the sulphuric acid and potassa has combined, and the compound removed by crystallization. If the difference in solubility is considerable, the separation of salts may be often rendered very complete by this method.

The efflorescence of a salt is sometimes attended with a similar result. If carbonate of soda and muriate of lime are mingled together in solution, double decomposition takes place, and the insoluble carbonate of lime subsides. But if carbonate of lime and sea-salt are mixed in the solid state, and a certain degree of moisture is present, a mutual interchange of the constituents ensues. Carbonate of soda, and muriate of lime, are slowly generated; and as the former, as soon as it is formed, separates itself from the mixture by efflorescence, its production continues progressively. The efflorescence of carbonate

of soda, which is sometimes seen on old walls, or which in some countries is found on the soil, appears to have originated in this manner.

## *Elasticity.*

From the obstacle which cohesion puts in the way of affinity, the gaseous state in which the cohesive power is wholly wanting, might be expected to be peculiarly favourable to chemical action. The reverse, however, is the fact. Bodies evince little disposition to unite when presented to each other in the elastic form. Combination does indeed sometimes take place, in consequence of a very energetic attraction; but examples of an opposite kind are much more common. Oxygen and hydrogen gases, and chlorine and hydrogen, though their mutual affinity is very powerful, may be preserved together for any length of time without combining. This want of action seems to arise from the distance between the particles preventing that close approximation which is so necessary to the successful exercise of affinity. Hence many gases cannot be made to unite directly, which nevertheless combine readily while in their *nascent* state; that is, while in the act of assuming the gaseous form by the decomposition of some of their solid or fluid combinations.

Elasticity operates likewise as a decomposing agent. If two gases, whose reciprocal attraction is feeble, suffer considerable condensation when they unite, the compound will be decomposed by very slight causes. The chloride of nitrogen, which is an oily-like liquid, composed of the two gases, chlorine and nitrogen, answers this description completely; and it is remarkable for being the most explosive substance hitherto discovered. A slight elevation of temperature, by increasing the natural elasticity of the two gases, or the contact of substances which have an affinity for either of them, produces an immediate explosion.

Many familiar phenomena of decomposition are owing to elasticity. All compounds that contain a volatile and a fixed principle, are liable to be decomposed by a high temperature. The expansion occasioned by caloric removes the elements of the compound to a greater distance from one another, and thus, by diminishing the force of chemical attraction, favours the tendency of the volatile principle to assume the form which is natural to it. The evaporation of water from a solution of salt is an instance of this kind.

Many solid substances which contain water in a state of intimate combination, part with it in a strong heat, in consequence of the volatile nature of that liquid. The separation of oxygen from some metals, by heat alone, is explicable on the same principle.

It appears from these, and some preceding remarks, that the influence of caloric over affinity is variable; for at one time it promotes chemical union, and opposes it at another. Its action, however, is always consistent. Whenever the cohesive power is an obstacle to combination, caloric favours affinity, as by diminishing the cohesion of a solid, or by converting a solid into a liquid. As the cause of the gaseous state, on the contrary, it keeps at a distance particles which would otherwise unite; or by producing expansion, it tends to separate substances from one another, which are already combined. There is one effect of caloric which seems somewhat anomalous; namely, the combination which ensues in gaseous explosive mixtures on the approach of flame. The explanation given by Berthollet is probably correct,—that the sudden dilatation of the gases in the immediate vicini-

ty of the flame, acts as a violent compressing power to the contiguous portions, and thus brings them within the sphere of their attraction.

Some of the decompositions, which were attributed by Bergmann to the sole influence of elective affinity, may be ascribed to elasticity. If three substances are mixed together, two of which can form a compound which is less volatile than the third body, the last will, in general, be completely driven off by the application of heat. The decomposition of the muriate or any of the salts of ammonia, by lime or the pure alkalies or alkaline earths, may be adduced as an example ; and for the same reason, all the carbonates are decomposed by muriatic acid, and all the muriates by sulphuric acid. This explanation applies equally well to some cases of double decomposition. It explains, for instance, why the dry carbonate of lime will decompose muriate of ammonia by the aid of heat; for carbonate of ammonia is more volatile than the muriate either of ammonia or lime.

The influence of elasticity in determining the result of chemical action in these instances, seems owing to the same cause which enables insolubility to be productive of similar effects. Thus on mixing muriate of ammonia, and lime, the acid is divided between the two bases, some ammonia becomes free, which, in consequence of its elasticity, is entirely expelled by a gentle heat. The acid of the remaining muriate of ammonia is again divided between the two bases; and if a sufficient quantity of lime is present, the ammoniacal salt will be completely decomposed. In like manner the decomposition of potassa may be effected by iron, though the affinity of this metal for oxygen seems much inferior to that of potassium for oxygen. If potassa in the fused state be brought in contact with metallic iron at a white heat, the oxygen is divided between the two metals, and a portion of potassium set at liberty. But as potassium is volatile at a white heat, it is expelled at the instant of reduction, and thus by its influence being withdrawn gives an opportunity for the decomposition of an additional quantity of potassa.

## *Quantity of Matter.*

The influence of quantity of matter over affinity is universally admitted. If one body A unites with another body B in several proportions, that compound will be most difficult of decomposition which contains the smallest quantity of B. Of the three oxides of lead, for instance, the peroxide parts most easily with its oxygen by the action of caloric; a higher temperature is required to decompose the deutoxide, and the protoxide will bear the strongest heat of our furnaces, without losing a particle of its oxygen.

The influence of quantity over chemical attraction may be further illustrated by the phenomena of solution. When equal weights of a soluble salt are added in succession to a given quantity of water, which is capable of dissolving almost the whole of the salt employed, the first portion of the salt will disappear more readily than the second, the second than the third, the third than the fourth, and so on. The affinity of the water for the saline substances diminishes with each addition, till at last it is weakened to such a degree as to be unable to overcome the cohesion of the salt. The process then ceases, and a saturated solution is obtained.

Quantity of matter is employed advantageously in many chemical operations. If, for instance, a chemist is desirous of separating an acid from a metallic oxide by means of the superior affinity of potassa

for the former, he frequently uses rather more of the alkali than is sufficent for neutralizing the acid. He takes the precaution of employing an excess of alkali, in order the more effectually to bring every particle of the substance to be decomposed in contact with the decomposing agent.

But Berthollet has attributed a much greater influence to quantity of matter. It was the basis of his doctrine, developed in the *Statique Chimique*, that bodies cannot be wholly separated from each other by the affinity of a third substance for one element of a compound; and to explain why a superior chemical attraction does not produce the effect which might be expected from it, he contended that quantity of matter compensates for a weaker affinity. From the cooperation of several disturbing causes, Berthollet perceived that the force of affinity cannot be estimated with certainty by observing the order of decomposition; and he therefore had recourse to another method. He set out by supposing that the affinity of different acids for the same alkali, is in the inverse ratio of the ponderable quantity of each which is necessary for neutralizing equal quantities of the alkali. Thus, if two parts of one acid A, and one part of another acid B, are required to neutralize equal quantities of the alkali C, it was inferred that the affinity of B for C was twice as great as that of A. He conceived, further, that as two parts of A produce the same neutralizing effect as one part of B, the attraction exerted by any alkali towards two parts of A ought to be precisely the same as for the one part of B; and he hence concluded that there is no reason why the alkali should prefer the small quantity of one to the large quantity of the other. On this he founded the principle that quantity of matter compensates for force of attraction.

Berthollet has here obviously confounded two things, namely, force of attraction and neutralizing power, which are really different, and ought to be held distinct. The relative weights of muriatic and sulphuric acids required to neutralize an equal quantity of any alkali, or, in other words, their capacities of saturation, are as 37 to 40, a ratio which remains constant with respect to all other alkalies. The affinity of these acids, according to Berthollet's rule, will be expressed by the same numbers. But in taking this estimate, we have to make three assumptions, all of which are disputable. There is no proof, in the first place, that muriatic acid has a greater affinity for an alkali, such as potassa, than sulphuric acid. Such an inference would be directly opposed to the general opinion founded on the order of decomposition; and though that order, as has been shown, is by no means a satisfactory test of the strength of affinity, it would be improper to adopt an opposite conclusion without having good reasons for doing so. Secondly, were it established that muriatic acid has the greater affinity, it does not follow that the attraction of those acids for potassa is in the ratio of 37 to 40. And, thirdly, supposing this point settled, it is very improbable that the ratio of their affinity for one alkali will apply to all others; analogy would lead us to anticipate the reverse. Independently of these objections, M. Dulong has found that the principle of Berthollet is not in accord with the results of experiment.

Though this mode of determining the relative forces of affinity cannot be admitted, it is possible that quantity of matter may somehow or other compensate for a weaker affinity, and Berthollet attempted to prove it by experiment. On boiling the sulphate of baryta with an equal weight of pure potassa, the alkali is found to have deprived the baryta of a small portion of its acid; and on treating oxalate of lime with nitric acid, some nitrate of lime is generated. As these partial

decompositions are contrary to the supposed order of elective affinity, it was conceived that they were produced by quantity of matter acting in opposition to force of attraction. But they by no means justify such a conclusion. In the decomposition of sulphate of baryta by potassa*, no care was taken to exclude the atmospheric air during the operation: the alkali must consequently have absorbed carbonic acid; and it is an established fact that carbonate of potassa decomposes partially the sulphate of baryta. A similar omission appears to have been made in the other experiments where decomposition was attempted by pure potassa or soda. In many instances the result may fairly be attributed to other causes. Acids and alkalies have often a tendency to unite in more than one proportion, and will readily form salts with excess of acid or of base when circumstances are favourable to their production. Thus on adding nitric acid to the insoluble phosphate of lime, the earth is divided between the two acids, and a nitrate and bi-phosphate of lime are generated. It is difficult, if not impossible, to effect the entire decomposition of nitrate of potassa by a quantity of sulphuric acid just sufficient for neutralizing the alkali; for the sulphuric acid, instead of taking the whole of the potassa, is apt to unite with part of it, and form the bisulphate. This tendency to the formation of an acid salt accounts for the fact quite satisfactorily; nor is there any reason to infer the co-operation of any other cause. Another circumstance that influences the result of such experiments, and which Berthollet left out of view entirely, is the affinity of salts for one another. On the whole, therefore, we may infer that Berthollet has given no satisfactory case in which quantity of matter is proved to compensate for a weaker affinity. Saline substances, indeed, seem ill adapted to such researches. For it is impossible in many, if not in most cases, to decide upon the relative strength of the attraction of two acids for an alkali, or of two alkalies for an acid, which nevertheless is an important element in the inquiry; and even did we possess such knowledge, the influence of modifying circumstances is such, that it is difficult to appreciate the share they may have in producing a given effect.

## *Gravity.*

The influence of gravity is perceptible when it is wished to make two substances unite, the densities of which are different. In a case of simple solution, a larger quantity of saline matter is found at the bottom than at the top of the liquid, unless the solution shall have been well mixed subsequently to its formation. In making an alloy of two metals which differ from one another in density, a larger quantity of the heavier metal will be found at the lower than in the upper part of the compound, unless great care be taken to counteract the tendency of gravity by agitation. This force obviously acts, like the cohesive power, in preventing a sufficient degree of approximation.

## *Imponderables.*

The influence which caloric exerts over chemical phenomena, and the modes in which it operates, have been already discussed. The chemical agency of galvanism has also been described. The effects of light will be most conveniently stated in other parts of the work.

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* Researches into the Laws of Affinity.

Electricity is frequently employed to produce the combination of gases with one another, and in some instances to separate them. It appears to act by the heat which it occasions, and therefore on the same principle as flame.

## *On the Measure of Affinity.*

As the foregoing observations prove that the order of decomposition is not always a satisfactory measure of affinity, it becomes a question whether there are any means of determining the comparative forces of chemical attraction. When no disturbing causes operate, the phenomena of decomposition afford a sure criterion; but when the conclusions obtained in this way are doubtful, assistance may be frequently derived from other sources. The surest indications are procured by observing the tendency of different substances to unite with the same principle, under the same circumstances, and subsequently by marking the comparative facility of decomposition when the compounds so formed are exposed to the same decomposing agent. Thus, on exposing gold, lead, and iron, to air and moisture, the iron rusts with great rapidity, the lead is only tarnished, and the gold retains its lustre. It is hence inferred that iron has the greatest affinity for oxygen, lead next, and gold least. This conclusion is supported by concurring observations of a like nature, and confirmed by the circumstances under which the oxides of those metals part with their oxygen. The oxide of gold is reduced by heat only; and the oxide of lead is decomposed by charcoal at a lower temperature than the oxide of iron.

It is inferred from the action of caloric on the carbonates of potassa, baryta, lime, and the oxide of lead, that potassa has a stronger attraction for carbonic acid than baryta, bartya than lime, and lime than the oxide of lead. The affinity of different substances for water may be determined in a similar manner.

Of all chemical substances, our knowledge of the relative degrees of attraction of the acids and alkalies for each other is the most uncertain. Their action on one another is affected by so many circumstances, that it is in most cases impossible, with certainty, to refer any effect to its real cause. The only methods that have been hitherto devised for remedying this defect are those of Berthollet and Kirwan. Both of them are founded on the capacities of saturation, and the objections which have been urged to the rule suggested by the first philosopher, apply equally to that proposed by the second. But this uncertainty is of no great consequence in practice. We know perfectly the order of decomposition, whatever may be the actual forces by which it is effected.

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# SECTION II.

## *ON THE PROPORTIONS IN WHICH BODIES UNITE, AND ON THE LAWS OF COMBINATION.*

The study of the proportions in which bodies unite naturally resolves itself into two parts. The first includes compounds whose elements appear to unite in a great many proportions; the second comprehends those, the elements of which combine in a few proportions only.

I. The compounds contained in the first division are of two kinds. In one, combination takes place unlimitedly in all proportions; in the other, it occurs in every proportion within a certain limit. The union of water with alcohol and the liquid acids, such as the sulphuric, muriatic, and nitric acids, are instances of the first mode of combination; the solutions of salts in water are examples of the second. One drop of sulphuric acid may be diffused through a gallon of water, or a drop of water through a gallon of the acid; or they may be mixed together in any intermediate proportions, and in each case they appear to unite perfectly with one another. A hundred grains of water, on the contrary, will dissolve any quantity of sea-salt which does not exceed forty grains. Its dissolving power then ceases, because the cohesion of the solid becomes comparatively too powerful for the force of affinity. The limit to combination is in such instances owing to the cohesive power; and but for the obstacle which it occasions, the salt would most probably unite with the water in every proportion.

All the substances that unite in many proportions, give rise to compounds which have this common character, that their elements are united by a feeble affinity, and preserve, when combined, more or less of the properties which they possess in a separate state. In a scientific point of view, these combinations are of minor importance; but they are exceedingly useful as instruments of research. They enable the chemist to present bodies to one another, under the most favourable circumstances possible for acting with effect; the liquid form is thus communicated to them, while the affinity of the solvent or menstruum, which holds them in solution, is not sufficiently powerful to interfere with their attraction for one another.

II. The most interesting series of compounds is produced by substances which unite in a few proportions only; and which, in combining, lose more or less completely the properties that distinguished them when separate. Of these bodies, some form but one combination. Thus there is only one compound of zinc and oxygen, or of chlorine and hydrogen. Others combine in two proportions. For example, two compounds are formed by copper and oxygen, or by hydrogen and oxygen. Other bodies again unite in three, four, five, or even six proportions, which is the greatest number of compounds that any two substances are known to produce, excepting those which belong to the first division.

The combination of substances that unite in a few proportions only, is regulated by three remarkable laws. The first of these laws is, that the composition of bodies is fixed and invariable; that a compound substance, so long as it retains its characteristic properties, must always consist of the same elements united together in the same proportion. Sulphuric acid, for example, is always composed of sulphur and oxygen in the ratio of 16 parts* of the former to 24 of the latter; no other elements can form it, nor can its own elements form it in any other proportion. Water, in like manner, is formed of 1 part of hydrogen and 8 of oxygen; and were these two elements to unite in any other proportion, some new compound, different from water, would be the product. The same observation applies to all other substances, however complicated, and at whatever period they were produced. Thus, sulphate of baryta, whether formed ages ago by the hand of nature, or quite recently by the operations of the chemist, is always composed of 40 parts of sulphuric acid and 78 of baryta. This law, in

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* By the expression 'parts' I always mean parts by weight.

fact, is universal and permanent. Its importance is equally manifest. It is the essential basis of chemistry, without which the science itself could have no existence.

Two views have been proposed by way of accounting for this law. The explanation now universally given is confined to a mere statement, that substances are disposed to combine in those proportions to which they are so strictly limited, in preference to any others; it is regarded as an ultimate fact, because the phenomena are explicable on no other known principle. A different doctrine was advanced by the celebrated Berthollet in his *Statique Chimique*, published in 1803. Having observed the influence of cohesion and elasticity in modifying the action of affinity as already described, he thought he could trace the operations of the same cause in producing the effect at present under consideration. Finding that the solubility of a salt and of a gas in water is limited, in the first by cohesion, and in the second by elasticity, he conceived that the same force would account for the unchangeable composition of certain compounds. He maintained, therefore, that within certain limits bodies have a tendency to unite in every proportion; and that combination is never definite and invariable, except when rendered so by the operation of modifying causes, such as cohesion, insolubility, elasticity, quantity of matter, and the like. Thus, according to Berthollet, sulphate of baryta is composed of 40 parts of sulphuric acid and 78 of baryta, not because those substances are disposed to unite in that ratio rather than in another, but because the compound so constituted happens to have great cohesive power.

These opinions which, if true, would shake the whole science of chemistry to its foundation, were founded on observation and experiment, supported by all the ingenuity of that highly gifted philosopher. They were ably and successfully combated by Proust, in several papers published in the *Journal de Physique*, wherein he proved that the metals are disposed to combine with oxygen and with sulphur only in one or two proportions, which are definite and invariable. The controversy which ensued between these eminent chemists on that occasion, is remarkable for the moderation with which it is conducted on both sides, and has been properly quoted by Berzelius as a model for all future controversialists. How much soever opinion may have been divided upon this important question at that period, the dispute is now at an end. The infinite variety of new facts, similar to those observed by Proust, which have since been established, has proved beyond a doubt that the leading principle of Berthollet is quite erroneous. The tendency of bodies to unite in definite proportions only, is indeed so great as to excite a suspicion that all substances combine in this way; and that the exceptions thought to be afforded by the phenomena of solution, are rather apparent than real; for it is conceivable that the apparent variety of proportion noticed in such cases may arise from the mixture of a few definite compounds with each other.

The second law of combination is still more remarkable than the first. It has given plausibility to an ingenious hypothesis concerning the ultimate particles of matter, called the *atomic theory*. The law itself, however, contains nothing hypothetical, being the pure expression of a fact, first noticed by Mr. Dalton, and subsequently confirmed by many other chemists. Its nature will be at once understood by a simple perusal of the following table:—

| | | | |
|---|---|---|---|
| Water is composed of | Hydrogen | 1 | Oxygen 8 |
| Deutoxide of Hydrogen | Do. | 1 | Do. 16 |
| Carbonic Oxide | Carbon | 6 | Do. 8 |
| Carbonic Acid | Do. | 6 | Do. 16 |
| Nitrous Oxide | Nitrogen | 14 | Do. 8 |
| Nitric Oxide | Do. | 14 | Do. 16 |
| Hyponitrous Acid | Do. | 14 | Do. 24 |
| Nitrous Acid | Do. | 14 | Do. 32 |
| Nitric Acid | Do. | 14 | Do. 40 |

Now it will be perceived, that in all these compounds the numbers denoting the oxygen, which is attached to a given weight of the same substance, bear a very simple ratio to one another. The deutoxide of hydrogen contains just twice as much oxygen as water does. The oxygen in carbonic acid is double that of carbonic oxide. The oxygen in the compounds of nitrogen and oxygen is in the ratio of 1, 2, 3, 4, and 5. So obvious indeed is this law, that it is observed at once on comparing together the results of a few accurate analyses; and the only subject of surprise is, that it was not discovered before. It is by no means confined to the compounds of combustibles with oxygen. Thus the sulphur in the two sulphurets of mercury, the chlorine in the two chlorides of mercury, are as 1 to 2. It extends also to the salts. The bicarbonate of potassa, for example, contains twice as much carbonic acid as the carbonate; and the oxalic acid of the three oxalates of potassa is in the ratio of 1, 2, and 4. We must regard it therefore as a law which regulates the union of bodies, and the enunciation of which may be stated in the following terms. When two substances, A and B, unite chemically in two or more proportions, the numbers representing the quantities of B combined with the same quantity of A are in the ratio of 1, 2, 3, 4, &c; that is, they are multiples by some whole number of the smallest quantity of B with which A can unite. Thus, if A+B is the first compound, the others will be A+2 B, or A+3 B, or A with some similar multiple of B. This law is often called the *law of multiples*, or of combination in *multiple proportions*.

That the elements of compounds are very generally arranged according to the law of multiples, does not admit of the least question; but in the present state of chemical science, we are not prepared to say that it is altogether universal. Instances are not unfrequently met with, where a slight deviation from the law appears to occur. The three oxides of lead, for instance, are thus constituted :—

| | *Lead.* | *Oxygen.* |
|---|---|---|
| Protoxide | 104 | 8 |
| Deutoxide | 104 | 12 |
| Peroxide | 104 | 16 |

In these compounds the oxygen is as 1 : 1½ : 2; and the oxides of manganese afford a similar example. The oxides of iron are composed as follows:—

| | *Iron.* | *Oxygen.* |
|---|---|---|
| Protoxide | 28 | 8 |
| Peroxide | 28 | 12 |

in which the ratio of the oxygen is as 1 to 1½ or as 2 to 3. The oxygen of the arsenious and arsenic acids, according to Berzelius, is as 3 to 5. It is obvious that these deviations from the law of multiples may perhaps be rather apparent than real. It is possible, for example, that the deutoxide of lead may be a compound of the protoxide

and peroxide of lead with each other, and therefore ought not to be enumerated among the oxides of that metal. It is also possible that the anomaly is frequently owing to our ignorance of compounds which may hereafter be discovered. Thus the discovery of an oxide of lead consisting of 104 parts of metal to 4 parts of oxygen, would render this series of compounds conformable to the usual law of combination. But leaving these points to be decided by future observation, and taking facts as they are, we may state that bodies combine either strictly according to the law of multiple proportion as first stated, or according to the slight deviation from that law as illustrated in the preceding examples. In either case this law of combination is exceedingly simple.

The third law of combination is intimately connected with the preceding, and is not less remarkable. Its existence and nature will at once appear on a comparison of the relative quantities of different bodies, which combine together. Thus 8 parts of oxygen unite with 1 part of hydrogen, 16 of sulphur, 36 of chlorine, 40 of selenium, and 110 parts of silver. Such are the quantities of these five bodies which are disposed to unite with 8 parts of oxygen; and it is found that when they combine with one another, they unite either in the proportions expressed by those numbers, or in multiples of them according to the law already explained. Thus sulphuretted hydrogen is composed of 1 part of hydrogen and 16 of sulphur, and bisulphuretted hydrogen of 1 part of hydrogen to 32 of sulphur; 36 of chlorine unite with 1 of hydrogen, 16 of sulphur, and 110 of silver; and 40 parts of selenium with 1 of hydrogen, and 16 of sulphur.

It is manifest, from these examples, that bodies unite according to proportional numbers; and hence has arisen the use of certain terms, such as Proportion, Combining Proportion, Proportional, or Equivalent, to express them. Thus the combining proportions of the substances just alluded to are

| | |
|---|---|
| Hydrogen . . . | 1 |
| Oxygen . . . | 8 |
| Sulphur . . . | 16 |
| Chlorine . . . | 36 |
| Selenium . . . | 40 |
| Silver . . . | 110 |

The most common kind of combination is one proportion of one body either with one or with two proportions of another. Combinations of one to three, or one to four, are very uncommon, unless the more simple compounds likewise exist. Ammonia, however, is a singular instance of the reverse. It is composed of 14 parts of nitrogen, and 3 of hydrogen. Now 14 being the precise quantity of nitrogen that unites with 8 of oxygen, is considered as one proportion of nitrogen, and this quantity is combined in ammonia with three proportionals of hydrogen. No compound of nitrogen and hydrogen in any other proportion has as yet been discovered. In some cases it appears that bodies unite in the ratio of two equivalents of one body to three or five equivalents of the other. There is good reason to believe that the hyposulphuric acid is constituted in this manner; and Berzelius is of opinion that this kind of arrangement is by no means unfrequent.

But this law does not apply to elementary substances only, since compound bodies have their combining proportions which may likewise be expressed in numbers. Thus since water is composed of one proportion or 8 parts of oxygen, and one proportion or 1 of hydrogen,

its combining proportion or equivalent is 9. The proportional of sulphuric acid is 40, because it is a compound of one proportion or 16 of sulphur, and three proportions or 24 of oxygen; and in like manner, the combining proportion of muriatic acid is 37, because it is a compound of one proportion or 36 of chlorine, and one proportion or 1 of hydrogen. The equivalent number of potassium is 40, and as that quantity combines with 8 of oxygen to form potassa, the combining proportion of potassa is 48. Now when these compounds unite, one proportion of the one combines with one, two, three, or more proportions of the other, precisely as the simple substances do. The hydrate of potassa, for example, is constituted of 48 parts of potassa and 9 of water, and its combining proportion is consequently 48+9, or 57. The sulphate of potassa is composed of 40 sulphuric acid+48 potassa; and the muriate of the same alkali of 37 muriatic acid+48 potassa. The combining proportion of the former salt is therefore 88, and of the latter 85.

The composition of the salts affords a very neat illustration of this subject; and to exemplify it still further, I subjoin a list of the proportional numbers of a few acids and alkaline bases.

| | | | |
|---|---|---|---|
| Hydrofluoric Acid | 19.86 | Lithia | 18 |
| Phosphoric Acid | 35.71 | Magnesia | 20 |
| Muriatic Acid | 37 | Lime | 28 |
| Sulphuric Acid | 40 | Soda | 32 |
| Nitric Acid | 54 | Potassa | 48 |
| Arsenic Acid | 58 | Strontia | 52 |
| | | Baryta | 78 |

It will be seen at a glance, that the neutralizing power of the different alkalies is very different; for the proportion of each base expresses the precise quantity required to neutralize a proportion of each of the acids. Thus 18 of lithia, 32 of soda, and 78 of baryta, combine with 19.86 of hydrofluoric acid, forming the neutral hydrofluates of lithia, soda and baryta. The same fact is obvious with respect to the acids; for 35.71 of phosphoric, 40 of sulphuric, and 58 of arsenic acid unite with 28 of lime, forming a neutral phosphate, sulphate and arseniate of lime.

These circumstances afford a ready explanation of a curious fact, first noticed by the Saxon chemist Wenzel;—when two neutral salts mutually decompose one another, the resulting compounds are likewise neutral. The cause of this fact is now obvious. If 88 parts of neutral sulphate of potassa are mixed with 132 of the nitrate of baryta, the 78 parts of baryta unite with the 40 of sulphuric acid, and the 54 parts of nitric acid of the nitrate combine with the 48 of potassa of the sulphate, not a particle of acid or alkali remaining in an uncombined condition.

| *Sulphate of Potassa.* | | *Nitrate of Baryta.* | |
|---|---|---|---|
| Sulphuric acid | 40 | 54 | Nitric acid |
| Potassa . | 48 | 78 | Baryta |
| | 88 | 132 | |

It matters not whether more or less than 88 parts of sulphate of potassa are added; for if more, a small quantity of sulphate of potassa will remain in solution; if less, nitrate of baryta will be in excess; but in either case the neutrality will be unaffected.

The utility of being acquainted with these important laws is almost too manifest to require mention. Through their aid, and by remem-

bering the proportional numbers of a few elementary substances, the composition of an extensive range of compound bodies may be calculated with facility. By knowing that 6 is the combining proportion of carbon and 8 of oxygen, it is easy to recollect the composition of carbonic oxide and carbonic acid; the first consisting of 6 parts of carbon +8 of oxygen, and the second of 6 carbon+16 oxygen. 40 is the equivalent of potassium, and potassa being its protoxide, is composed of 40 potassium+8 oxygen. From these few data, we know at once the composition of the carbonate and bicarbonate of potassa. The first is composed of 22 carbonic acid+48 potassa; the second of 44 carbonic acid+48 potassa. This knowledge is retained with very little effort of the memory; and the assistance derived from the method will be manifest on comparing it with the common practice of stating the composition in 100 parts.

| | *Carbonic Oxide.* | *Carbonic Acid.* |
|---|---|---|
| Carbon | 42.86 | 27.27 |
| Oxygen | 57.14 | 72.73 |
| | *Carbonate of Potassa.* | *Bicarbonate of Potassa.* |
| Carbonic acid | 31.43 | 47.83 |
| Potassa | 68.57 | 52.17 |

From the same data, calculations, which would otherwise be difficult or tedious, may be made rapidly and with ease, without reference to books, and frequently by a simple mental process. The exact quantities of substances required to produce a given effect may be determined with certainty, thus affording information which is often necessary to the success of chemical processes, and of great consequence both in the practice of the chemical arts, and in the operations of pharmacy.

The same knowledge affords a good test to the analyst by which he may judge of the accuracy of his result, and even sometimes correct an analysis which he has not the means of performing with rigid precision. Thus a powerful argument for the accuracy of an analysis is derived from the correspondence of its result with the laws of chemical union. On the contrary, if it form an exception to them, we are authorized to regard it as doubtful, and may hence be led to detect an error, the existence of which might not otherwise have been suspected. If an oxidized body is found to contain one proportion of the combustible with 7.99 of oxygen, it is fair to infer that 8, or one proportion of oxygen would have been the result, had the analysis been perfect.

The composition of a substance may sometimes be determined by a calculation founded on the laws of chemical union before an analysis of it has been accomplished. When the new alkali lithia was first discovered, chemists did not possess it in sufficient quantity for determining its constitution analytically. But the neutral sulphates of the alkalies and earths are known to be composed of one proportion of each constituent, and the oxides to contain one proportion of oxygen. If it be found, therefore, by analysis, that the neutral sulphate of lithia is composed of 40 parts of sulphuric acid and 18 of lithia, it may be inferred, since 40 is one proportion of the acid, that 18 is the equivalent for lithia, and that the oxide is formed of 8 parts of oxygen and 10 of lithium.

The method of determining the proportional numbers will be anticipated from what has already been said. The commencement is made by carefully analyzing a definite compound of two simple substances

which possess an extensive range of affinity. No two bodies are better adapted for this purpose than oxygen and hydrogen, and that compound is selected which contains the smallest quantity of oxygen. Water is such a substance, and it is therefore regarded as a compound of one proportion of oxygen to one proportion of hydrogen. But analysis proves that it is composed of 8 parts of the former to one of the latter, and therefore the equivalent of oxygen is eight times as heavy as that of hydrogen.

Some compounds are next examined, which contain the smallest proportion of oxygen or hydrogen in combination with some other substance. Carbonic oxide with respect to carbon, and sulphuretted hydrogen with respect to sulphur, answer this description perfectly. The former consists of 8 parts of oxygen and 6 of carbon; the latter of 1 part of hydrogen and 16 of sulphur. The proportional number of carbon is consequently 6, and of sulphur 16. The proportionals of all other bodies may be determined in the same manner.

Since the proportional numbers merely express the relative quantities of different substances which combine together, it is in itself immaterial what figures are employed to express them. The only essential point is, that the relation should be strictly observed. Thus, we may make the combining proportion of hydrogen 10 if we please; but then oxygen must be 80, carbon 60, and sulphur 160. We may call hydrogen 100 or 1000, or, if it were desirable to perplex the subject as much as possible, some high uneven number might be selected, provided the due relation between the different numbers is faithfully preserved. But such a practice would effectually do away with the advantage I have ascribed to the use of the proportional numbers, and hence it is the object of every one to employ such simple ones, that their relation may be perceived by mere inspection. As the opinion of different chemists concerning the simplicity of numbers is somewhat at variance, we possess several series of them. Dr Thomson, for example, makes oxygen 1, so that hydrogen is eight times less than unity, or 0.125, carbon 0.75, and sulphur 2. Dr Wollaston, in his scale of chemical equivalents, fixes oxygen at 10, by which hydrogen is 1.25, carbon 7.5, and so on. According to Berzelius, oxygen is 100. And lastly, several other chemists, such as Dalton, Davy, Henry, and others, call hydrogen unity, and therefore oxygen 8. One of these series may easily be reduced to either of the others by an obvious and simple arithmetical process; and excepting that of Berzelius, whose numbers are inconveniently high for practice, it is not very material to which of them the preference is given. I have myself adopted the last, because, as it rarely contains fractional parts, it appears best adapted to the purpose of teaching.

## *On the Atomic Theory of Mr Dalton.*

The brief sketch which has been given of the laws of combination will, I trust, serve to set the importance of this department of chemical science in its true light. It is founded, as will have been seen, on experiment alone, and the laws which have been stated are the pure expression of fact. It is not necessarily connected with any speculation, and may be kept wholly free from it.

It is not uncommon for persons commencing the study of chemistry to entertain a vague notion that this department of the science comprehends something uncertain and hypothetical in its nature, and to be thus led to form an erroneous idea of its importance. This misapprehension may easily be traced to its source. It was impossible to

reflect on the regularity and constancy with which bodies obey the laws of combination, without speculating about the cause of that regularity; and consequently, the facts themselves were no sooner noticed, than an attempt was made to explain them. Accordingly, when Mr Dalton published his discovery of those laws, he at once incorporated the description of them with his notion of their physical cause; and even expressed the former in language suggested by the latter. Since that period, though several British chemists of eminence, and in particular Dr Wollaston and Sir H. Davy, have recommended and practised an opposite course, both subjects have been but too commonly comprised under the name of atomic theory; and hence it has often happened that beginners have rejected the whole as hypothetical, because they could not satisfactorily distinguish those parts that are founded on fact, from those which are conjectural. All such perplexity would have been avoided, and this department of the science have been far better understood, and its value more justly appreciated, had the discussion concerning the atomic constitution of bodies been always kept distinct from what it is intended to explain. When employed in this limited sense, the atomic theory may be discussed in a few words.

Two opposite opinions have long existed concerning the ultimate elements of matter. It is supposed, according to one party, that every particle of matter, however small, may be divided into smaller portions, provided our instruments and organs were adapted to the operation. Their opponents contend, on the other hand, that matter is composed of certain atoms which are of such a nature as not to admit of division. These opposite opinions have from time to time been keenly contested, and with variable success, according to the acuteness and ingenuity of their respective champions. But it was at last perceived that no positive data existed capable of deciding the question, and its interest therefore gradually declined. The progress of modern chemistry has revived the general attention to this controversy, by affording a far stronger argument in favour of the atomic constitution of bodies than was ever advanced before, and which I conceive is almost irresistible. We have only in fact to assume with Mr Dalton, that all bodies are composed of ultimate atoms, the weight of which is different in different kinds of matter, and we explain at once the foregoing laws of chemical union. The phenomena do not appear explicable on any other supposition.

According to the atomic theory every compound is formed of the atoms of its constituents. An atom of A may unite with 1, 2, 3, or more atoms of B. Thus, supposing water to be composed of one atom of hydrogen and one atom of oxygen, the deutoxide of hydrogen will consist of one atom of hydrogen to two atoms of oxygen. If carbonic oxide is formed of one atom of carbon and one atom of oxygen, carbonic acid will consist of one atom of carbon to two atoms of oxygen. If in the compounds of nitrogen and oxygen enumerated at page 117, the first or protoxide is constituted of one atom of nitrogen to one atom of oxygen, the four others will be regarded as compounds of one atom of nitrogen to 2, 3, 4, and 5 atoms of oxygen. From these instances it will appear, that the law of multiple proportion is a necessary consequence of the atomic theory. There is also no apparent reason why two or more atoms of one substance may not combine with 2, 3, 4, 5, or more atoms of another. Such combinations will account for the complicated proportion noticed in some compounds, especially in many of those belonging to the animal and vegetable kingdoms.

In consequence of the very complete explanation which the laws of chemical union receive by means of the atomic theory, it has become customary to employ the term *atom* in the same sense as combining proportion or equivalent. For example, instead of saying water is composed of one equivalent of oxygen and one equivalent of hydrogen, it is said to consist of one atom of each element. In like manner sulphate of potassa is formed of one equivalent or one atom of sulphuric acid and one atom of potassa, the word in this case denoting as it were a compound atom, that is, the smallest integral particle of the acid or alkali; such a particle, which does not admit of being divided, except by the separation of its elementary or constituent atoms. The numbers expressing the proportions in which bodies unite, must likewise indicate, consistently with this view, the relative weights of atoms; and accordingly these numbers are often called *atomic weights*. Thus as water is composed of eight parts of oxygen and one of hydrogen, it follows, on the supposition of water consisting of one atom of each element, that an atom of oxygen must be eight times as heavy as an atom of hydrogen. If carbonic oxide is formed of an atom of carbon and an atom of oxygen, the relative weights of their atoms are as 6 to 8; and in short the relative weights of the atoms of all other bodies are expressed by the numbers which denote their combining proportions.

Though the phenomena of chemical combination leave little doubt of the atomic constitution of matter, other powerful arguments may now be adduced in favour of this theory. Dr Wollaston, in his Essay on the Finite Extent of the Atmosphere, (Philos. Trans. for 1822) has supported this doctrine on a new and independent principle, the particulars of which will be stated in the section on nitrogen. Another argument, which amounts almost to demonstration, is deducible from the peculiar connection noticed by Professor Mitscherlich between the form and composition of certain substances, a subject which will be discussed under the head of crystallization.

But in adopting the notion that matter is composed of ultimate individual particles, I am by no means satisfied of the propriety of expressing the facts of the science in language founded on this theory; because though the elements of bodies be arranged atomically, we have no certain method of ascertaining, in the present state of chemistry, how many atoms are contained in any compound. This difficulty is particularly felt with respect to those series of compounds in which half a proportion occurs; for as the idea of half an atom is inconsistent with the atomic theory, such an arrangement of the atoms must be imagined, as shall avoid the occurrence of a fraction. The mode of accomplishing this object may be exemplified in reference to the oxides of lead and iron, the constituents of which were mentioned on a former occasion. (page 117.) The oxides of lead may either be regarded as composed, the protoxide of one atom of lead to one atom of oxygen, the deutoxide of two atoms of lead to three atoms of oxygen, and the peroxide of one atom of lead to two atoms of oxygen; or they may be viewed as compounds, the protoxide of one atom of lead to two atoms of oxygen, the deutoxide of one atom of lead to three atoms of oxygen, and the peroxide of one atom of lead to four atoms of oxygen. In like manner the oxides of iron are either composed, the protoxide of one atom of iron and one atom of oxygen, and the peroxide of two atoms of iron to three atoms of oxygen; or the protoxide of one atom of iron to two atoms of oxygen, and the peroxide of one atom of iron to three atoms of oxygen. The uncertainty attending these atomic speculations cannot be more forcibly evinced than by

the fact, that Berzelius two or three years ago regarded all the stronger bases, such as the alkalies, alkaline earths, and the protoxides of several of the common metals, as composed of one atom of metal and two atoms of oxygen; but that he has suddenly abandoned this view, and now believes the very same substances to contain one atom of metal and one atom of oxygen. Such sudden changes cannot take place without producing material confusion; and tend to show that the science is not yet so far advanced as to admit of the atomic constitution of bodies being settled on permanent principles. Until the period when this desirable object may be accomplished, it is to be hoped that chemists will persevere in the practice, which is now universal in Britain, and adopted by several distinguished philosophers on the continent, of stating the combining proportions of bodies as nearly as possible in the way supplied by analysis, instead of doubling some numbers and halving others to make them conformable to some favourite hypothesis of the moment.

Mr Dalton supposes that the atoms of bodies are spherical, and has invented certain symbols to represent the mode in which he conceives they may combine together, as illustrated by the following figures.

⊙ Hydogen. ○ Oxygen.
⦶ Nitrogen. ● Carbon.

*Binary Compounds.*

○ ⊙ Water.
○ ● Carbonic oxide.

*Ternary Compounds.*

○ ⊙ ○ Deutoxide of hydrogen.
○ ● ○ Carbonic acid.
&c. &c. &c.

All substances containing only two atoms he called binary compounds, those composed of three atoms ternary compounds, of four, quaternary, and so on.

There are several questions relative to the nature of atoms, most of which will perhaps never be decided. Of this nature are the questions which relate to the actual form, size, and weight of atoms, and to the circumstances in which they mutually differ. All that we know with any certainty is, that their weights do differ, and by exact analysis the relations between them may be determined.

It is but justice to the memory of the late Mr Higgins of Dublin, to state that he first made use of the atomic hypothesis in chemical reasonings. In his "Comparative View of the phlogistic and antiphlogistic theories," published in the year 1789, he observes (pages 36 and 37) that "in volatile vitriolic acid, a single ultimate particle of sulphur is intimately united only to a single particle of dephlogisticated air; and that, in perfect vitriolic acid, every single particle of sulphur is united to two of dephlogisticated air, being the quantity necessary to saturation;" and he reasons in the same way concerning the constitution of water and the compounds of nitrogen and oxygen. These remarks of Mr Higgins do not appear to have had the slightest connection with the subsequent views of Mr Dalton. Indeed from facts which have come to my knowledge relating to the history of Mr Dalton's discovery, I am satisfied that this philosopher had not seen the work of Mr Higgins till after he had given an account of his own doctrine. The observations of Mr Higgins, therefore, though highly creditable to his sagacity, do not affect Mr Dalton's claim to originality.

They were made, moreover, in so casual a manner, as not only not to have attracted the notice of his contemporaries, but to prove that Mr Higgins himself attached no particular interest to them. Mr Dalton's real merit lies in the discovery of the Laws of Combination, a discovery which is solely and indisputably his; but in which he would have been anticipated by Mr Higgins, had that chemist perceived the importance of his own opinions.

## *On the Theory of Volumes.*

Soon after the publication of the New System of Chemical Philosophy in 1808, in which work Mr Dalton explained his views of the atomic constitution of bodies, a paper appeared in the second volume of the *Mémoires d'Arcueil*, by M. Gay-Lussac, on the "Combination of Gaseous Substances with one another." He there proved that gases unite together by volume in very simple and definite proportions. In the combined researches of himself and M. Humboldt, those gentlemen found that water is composed precisely of 100 measures of oxygen and 200 measures of hydrogen; and M. Gay-Lussac, being struck by this peculiarly simple proportion, was induced to examine the combinations of other gases with the view of ascertaining if any thing similar occurred in other instances.

The first compounds which he examined were those of ammoniacal gas with muriatic, carbonic, and fluoboric acid gases. 100 volumes of the alkali were found to combine with precisely 100 volumes of muriatic acid gas, and they could be made to unite in no other ratio. With both the other acids, on the contrary, two distinct combinations were possible. These are

| | | | |
|---|---|---|---|
| 100 | Fluoboric acid gas, with | 100 | Ammoniacal gas. |
| 100 | do. | 200 | do. |
| 100 | Carbonic acid gas | 100 | do. |
| 100 | do. | 200 | do. |

Various other examples were quoted, both from his own experiments and from those of others, all demonstrating the same fact. Thus ammonia was found by M. A. Berthollet to consist of 100 volumes of nitrogen and 300 volumes of hydrogen. 100 volumes of sulphurous acid and 50 volumes of oxygen produced sulphuric acid. Carbonic acid is composed of 50 volumes of oxygen and 100 volumes of carbonic oxide.

From these and other instances M. Gay-Lussac established the fact that gaseous substances unite in the simple ratio of 1 to 1, 1 to 2, 1 to 3, &c.; and this original observation has been confirmed by such a multiplicity of experiments, that it may be regarded as one of the best established laws in chemistry. Nor does it apply to the true gases merely, but to vapours likewise. For example, sulphuretted hydrogen, sulphurous acid, and hydriodic acid gases are composed of

| | | | |
|---|---|---|---|
| 100 vol. | hydrogen, and | 100 vol. | vapour of sulphur. |
| 100 | oxygen | 100 | . . sulphur. |
| 100 | hydrogen | 100 | . . iodine. |

There are very good grounds to suppose, also, that solid bodies which are fixed in the fire would, when in the form of vapour, be subject to the same law. By a method which will be explained afterwards, we may calculate what the specific gravity of carbon would be, if converted into vapour; and 0.4166 is the number so determined, atmospheric air being unity. Now, if we assume that carbonic acid is

formed of 100 volumes of oxygen, and 100 volumes of the vapour of carbon, condensed into the space of 100 volumes, the specific gravity of carbonic acid will be 1.1111 (the sp. gr. of oxygen) + 0.4166 = 1.5277, which is the precise number determined by experiment. Again, it follows from our assumption, that carbonic acid is composed by weight of

| | | | |
|---|---|---|---|
| Oxygen | 1.1111 | . | 16, or two proportionals. |
| Carbon | 0.4166 | . | 6, or one proportional. |

and this deduction is confirmed by analysis.

If we assume that carbonic oxide is composed of 50 volumes of oxygen and 100 volumes of the vapour of carbon, condensed into the space of 100 volumes, then its specific gravity will be 0.5555 (half the sp. gr. of oxygen) + 0.4166 = 0.9721; and its composition will be

| | | | |
|---|---|---|---|
| Oxygen | 0.5555 | . | 8, or one proportional. |
| Carbon | 0.4166 | . | 6, or one proportional. |

both of which results have been determined by other methods.

The compounds of carbon and hydrogen are equally illustrative of the same point. If light carburetted hydrogen is formed of 200 volumes of hydrogen and 100 volumes of the vapour of carbon, condensed into 100 volumes, its specific gravity should be 0.1388 (twice the sp. gr. of hydrogen) + 0.4166 = 0.5554; and its composition by weight will be

| | | | | |
|---|---|---|---|---|
| Hydrogen | . | 0.1388 | . . | 2, or two P. |
| Carbon | . | 0.4166 | . . | 6, or one P. |

If 100 volumes of olefiant gas are composed of 200 volumes of hydrogen and 200 volumes of the vapour of carbon, its specific gravity will be 0.1388 + 0.8332 = 0.9720; and its composition by weight must be

| | | | | |
|---|---|---|---|---|
| Hydrogen | . | 0.1388 | . . | 2, or two P. |
| Carbon | . | 0.8332 | . . | 12, or two P. |

I need hardly observe that both these results have been ascertained by analysis.

Another remarkable fact established by M. Gay-Lussac in the same paper is, that the diminution of bulk which gases frequently suffer in combining, is also in a very simple ratio. Thus, the 4 volumes of which ammonia is constituted, (3 volumes of hydrogen and 1 of nitrogen) contract to one-half or two volumes when they unite. There is a contraction to two-thirds in the formation of nitrous oxide gas. The same applies to the combination of gases and vapours. There is a contraction to a half in the formation of sulphuretted hydrogen; and to a half in that of sulphurous acid. The instances just quoted relative to the vapour of carbon confirm the same remark. There is a contraction to two-thirds in carbonic oxide; to a half in carbonic acid; to a third in light carburetted hydrogen; and to a fourth in olefiant gas.

The rapid progress which chemistry has made within the last few years is in great measure attributable to the ardour with which pneumatic chemistry has been cultivated. That very department which at first sight appears so obscure and difficult, has afforded a greater number of leading facts than any other; and the law of Gay-Lussac, by giving an additional degree of precision to such researches, as well as from its own intrinsic value, is one of the brightest discoveries that adorn the annals of the science. The practice of estimating the quantity in weight of any gas, by measuring its bulk or volume, of itself

susceptible of much accuracy, is rendered still more precise and satisfactory by the operation of this law. It will not perhaps be superfluous, therefore, to exemplify the method of reasoning employed in these investigations by a few examples; which will serve, moreover, as a useful specimen to the beginner of the nature of chemical proof.

One essential element in every inquiry of this kind, which is indeed the keystone of the whole, is a knowledge of the specific gravity of the gases. But it is exceedingly difficult to determine the specific gravity of gases with perfect accuracy; for not only do slight alterations of temperature and pressure during the experiment affect the result, but the presence of a little watery vapour, atmospheric air, or other impurity, may cause material error, especially when the gas to be weighed is either very light or very heavy. The specific gravity of important gases has, accordingly, been stated differently by different chemists, and there is none in regard to which more discordant statements of this fact have been made than of hydrogen gas. Fortunately we possess the power of correcting the results, and of estimating their accuracy by means of other data, upon which greater reliance may be placed. According to our best data, the specific gravity of oxygen, hydrogen, and nitrogen gases, air being 1, is

| | |
|---|---|
| Oxygen . . | 1.1111 |
| Hydrogen . . | 0.0694 |
| Nitrogen . . | 0.9722 |

It has been proved by analysis that 200 volumes of ammoniacal gas are composed of 300 volumes of hydrogen and 100 volumes of nitrogen, a fact from which the specific gravity of that alkali may be calculated.

$$\text{Thus, } 0.9722+(0.0694\times3)=1.1804$$

$\frac{1.1804}{4}=0.2951$, the specific gravity which ammoniacal gas should have, did its constituent gases suffer no contraction; but as they contract to one-half, the real specific gravity is double what it otherwise would be, or is 0.5902. Now, if by weighing a certain quantity of ammoniacal gas, the same number is procured for its specific gravity, it follows that all the elements of the calculation must have been correct.

Nitric oxide is composed of 100 volumes of nitrogen and 100 volumes of oxygen, united without any contraction, and forming, consequently, 200 volumes of the compound. Its specific gravity must, therefore, be the mean of its components, or $\frac{1.1111+0.9722}{2}=1.0416$. The coincidence of this calculated result with that determined by weighing the gas itself, proves that all the data are true. It is obvious, indeed, that the calculated results, as being free from the unavoidable errors of manipulation, must be the most accurate, provided the elements of the calculation may be trusted.

Dr Henry has proved by careful analysis that 100 volumes of light carburetted hydrogen gas, a compound of carbon and hydrogen, require 200 volumes of oxygen for complete combustion; that water and carbonic acid are the sole products; and that the latter amounts precisely to 100 volumes. From these data, the proportions of its constituents and its specific gravity may be determined. For 100 volumes of carbonic acid contain 100 volumes of the vapour of carbon, which must have been present in the carburetted hydrogen, and 100 volumes of oxygen. One-half of the oxygen originally employed is thus account-

ed for; and the remainder must have combined with hydrogen. But 100 volumes of oxygen require 200 volumes of hydrogen for combination, all of which must likewise have been contained in the carburetted hydrogen. The 100 volumes of light carburetted hydrogen, submitted to analysis, are hence composed of 100 volumes of the vapour of carbon, and 200 volumes of hydrogen. Its specific gravity must therefore be 0.5554; that is, 0.4166 (the sp. gr. of carbon vapour) +0.1388, or twice the sp. gr. of hydrogen gas.

Having ascertained that light carburetted hydrogen gas is composed of two measures of hydrogen to one of the vapour of carbon, it is easy to calculate the proportion of its constituents in weight. For this purpose we need only multiply the bulk of the gases by their respective specific gravities. Thus $200 \times 0.0694 = 13.88$, and $100 \times 0.4166 = 41.66$. Hence light carburetted hydrogen is composed by weight of

| | | |
|---|---|---|
| Carbon . . | 41.66 . | 6 |
| Hydrogen . . | 13.88 . | 2 |

The theory of volumes has very considerable resemblance to the laws of combination by weight developed by Mr Dalton; for the multiple proportions are as apparent in the former as in the latter. But there is one remarkable difference between them. The weights of the two elements of a compound have no apparent dependence on one another. Thus 6 parts of carbon and 8 of oxygen constitute carbonic oxide, and 8 parts of oxygen and 14 of nitrogen are contained in nitrous oxide; but eight is not a multiple by any whole number of 6, nor 14 of 8. On the other hand, the elements of a compound are always united by volume in the ratio of 1 to 1, 1 to 2, 1 to 3, and so on. This simple ratio is peculiarly interesting, because it appears to indicate a close correspondence in the size of the atoms of gaseous bodies. It naturally suggests the idea that this peculiarity may arise from the atoms of elementary principles possessing the same magnitude. On this supposition, equal measures of such substances in the gaseous form, at the same temperature and pressure, would probably contain an equal number of atoms; and the specific gravity of these gases would depend on the relative weights of their atoms. The same numbers which indicate the specific gravity of elementary principles in the gaseous state, would then express the relative weights of their atoms; so that the latter would be ascertained by means of the former, or the atomic weight of a solid or liquid represent the specific gravity of its vapour. The proportional numbers adopted by Sir H. Davy in his Elements of Chemical Philosophy, and the atomic weights employed by Berzelius in his System of Chemistry, were selected in accordance with this view. Thus water being formed of 2 measures of hydrogen and 1 measure of oxygen, is believed by Berzelius to consist of 2 atoms of the former and 1 atom of the latter; and for a similar reason, he regards the protoxide of nitrogen as a compound of 2 atoms of nitrogen and 1 atom of oxygen. The atoms and volumes of the four elementary gases, oxygen, chlorine, hydrogen, and nitrogen, are thus made to coincide with each other. This method, though perhaps preferable to any other, has not hitherto been generally followed. Most chemists consider water, protoxide of chlorine, and protoxide of nitrogen, as containing one atom of each of their elements; and, consequently, as these compounds consist of 1 measure of oxygen united with 2 measures of the other constituent, the atom of hydrogen, chlorine, and nitrogen is supposed

to occupy twice as much space as an atom of oxygen. An atom of oxygen is therefore represented by half a volume, and an atom of the other three gases by a whole volume.

Dr Prout in an ingenious essay "On the Relation between the Specific Gravities of Bodies in their Gaseous State and the Weights of their Atoms," published in the 6th volume of the Annals of Philosophy, (Old Series, p. 321,) considers it probable that the same relation which is thought to exist between the atoms and volumes of the four elementary gases, may hold equally of the vapours of the other elements. Thus in representing the atom of oxygen by half a volume, he believes the atoms of the other elementary principles, such as iodine, carbon, and sulphur, correspond to a whole volume of their vapour. From this he has deduced a mode of calculating the specific gravity of any vapour from the atomic weight of the body which yields it. The rule consists in multiplying 0.5555, or half the specific gravity of oxygen gas, by the atomic weight of any element, and dividing the product by the atomic weight of oxygen; the quotient is the specific gravity of the vapour. For example, the specific gravity of the vapour of carbon is thus found: As

$$8 : 6 : : 0.5555 : 0.4166$$

in which 8 is the atomic weight of oxygen, 6 that of carbon, and 0.4166 the specific gravity of the vapour of carbon. The same relation which exists between the atomic weight of oxygen and half its specific gravity, subsists between the atomic weight of any other element, and the specific gravity of its vapour. Though the accuracy of Dr Prout's views has not yet been established by experiment, his formula may often be employed with advantage.

In the essay above quoted, Dr Prout has advanced several instances, in which the equivalents or atomic weights of bodies appear to be multiples by a whole number of the atomic weight of hydrogen gas; and he threw out a conjecture that the same relation may perhaps exist in other cases. This subject has since been experimentally investigated by Dr Thomson, who has declared after a most elaborate inquiry, the fruits of which are contained in his "First Principles of Chemistry," that the law is of universal application; that the atomic weights of all the simple substances which he has examined are not only multiples by a whole number of the atomic weight of hydrogen, but with a few exceptions of two atoms of hydrogen. But in opposition to this statement, Berzelius insists that the law is inconsistent with the results of his analyses, and that the experiments of Dr Thomson are inaccurate. Considering the direct opposition of evidence, and the authority by which it is supported on both sides, we cannot but infer that the question is just as far from being decided as ever.

## *On the Theory of Berzelius.*

It is well known that the celebrated professor of Stockholm has for many years devoted himself to the study of the laws of definite proportions, and that he has been led to form a peculiar hypothesis, by way of generalizing the facts which his industry had collected. To give a detailed account of his system does not fall within the plan of this work; but considering the extraordinary number of facts with which this indefatigable chemist has enriched the science, and especially this department, I think it proper to give a short account of his doctrines, offering at the same time a few comments upon them.

Berzelius mentions in the historical introduction to his treatise on the "Theory of Definite Proportions," that he commenced his researches on the subject in the year 1807; and that they originated in the study of the Works of Richter. From Richter's explanation of the fact, that when two neutral salts decompose one another, the resulting compounds are likewise neutral, he perceived that one good analysis of a few salts would furnish the means of calculating the composition of all others. He accordingly entered upon an inquiry, which was at first limited in its object: but as he proceeded, his views enlarged, and advancing from one step to another, he at length set about determining the laws of combination in general. In perusing his account of the investigation, we are at a loss whether most to admire the number of exact analyses which he performed, the variety of new facts he determined, his acuteness in detecting sources of error, his ingenuity in devising new analytical processes, or the persevering industry which he displayed in every part of the inquiry. But it is at the same time impossible to suppress regret, that, instead of forming a complex system of his own, he did not adopt the simple views of Mr Dalton. This he might have done with very great propriety; since the fundamental laws which he discovered, are, with very little exception, either identical with those previously pointed out by the British philosopher, or the direct result of their operation.

Berzelius assumes, with Mr Dalton, the existence of ultimate indivisible atoms, to the combination of which with one another the laws of chemical proportion are owing.

The first law of Berzelius is the following. "One atom of one element unites with 1, 2, 3, or more atoms of another element." This coincides with the law of Mr Dalton, and requires no comment, further than that it has been amply confirmed by the labours of Berzelius. The second is, that "two atoms of one element combine with three and five atoms of another." These are the two laws which regulate the union of simple or elementary atoms.

The combination of compound atoms with each other, obeys another law, and is confined within still narrower limits. "Two compounds which contain the same electro-negative body, always combine in such a manner that the electro-negative element of the one is a multiple by a whole number of the same element of the other." Thus, for instance, if two oxidized bodies unite, the oxygen of one is a multiple by a whole number of the oxygen in the other. Various examples may be given of this. The hydrate of potassa is composed of

| | | | |
|---|---|---|---|
| Potassa | 48, | the oxygen of which is | 8. |
| Water | 9, | do | 8. |

In like manner, if two acids or two oxides combine, the same will be observed.

In the earthy minerals which often contain several oxides, the same law is found to prevail with great uniformity.

The composition of the salts is likewise under its influence. Carbonate of potassa, for example, is composed of

| | | | |
|---|---|---|---|
| Carbonic acid | 22, | the oxygen of which is | 16. |
| Potassa . | 48, | do | 8. |

and sulphate of potassa of

| | | | |
|---|---|---|---|
| Sulphuric acid | 40, | the oxygen of which is | 24. |
| Potassa . | 48, | do. | 8. |

Berzelius has remarked, that the nitrates, phosphates, and arseniates, may prove exceptions to the law in some instances. There is also a similar relation in salts which contain water of crystallization, between the oxygen of the base of the salt and that of the water. For instance, crystallized sulphate of soda is composed of

| | | | |
|---|---|---|---|
| Sulphuric acid | 40. | | |
| Soda . | 32, | the oxygen of which is | 8. |
| Water . | 90, | do | 80. |

Double salts are also influenced by the same law. In the tartrate of potassa and soda, for example, the oxygen of the potassa is exactly equal to the oxygen in the soda; and the oxygen in the tartaric acid, which neutralizes the potassa, is equal to that of the soda.

But this is not all that Berzelius has remarked with respect to the constitution of the salts. He observes that in each series of salts, the same relation always exists between the oxygen of the acid and of the base. In all the neutral sulphates this ratio is as three to one, as may be seen in the sulphates of soda and potassa. In the carbonates, the oxygen of the acid is double, and in the bicarbonates quadruple the oxygen of the base.

The existence of these remarkable laws was discovered by Berzelius at a very early period of his researches; and he mentions, that as subsequent observation, during the course of several years, has not afforded a single exception to them, he now regards them as universal. He accordingly places unlimited confidence in their accuracy, and is in the habit of calculating the composition of bodies on this principle.

It will of course be interesting to inquire into the cause of these phenomena; to ascertain if there is any property peculiar to oxygen, or other negative electrics, which may give rise to them. Berzelius himself says that "the cause is involved in such deep obscurity, that it is impossible at the present moment to give a probable guess at it." I have the misfortune to differ entirely from Berzelius on this question. So far from being obscure, it is perfectly intelligible, and is precisely what may be anticipated from the present state of chemical knowledge. Most of the salts called neutral sulphates, are composed of one proportion or one atom of sulphuric acid, and one proportion of some protoxide. This is the case with all the alkaline and earthy sulphates, and with several of the common metals, such as lead, zinc, and iron. Now, one proportion of sulpuric acid is composed of

Sulphur 16—one proportion.
Oxygen 24—three proportions.

and every protoxide of

Metal —one proportion.
Oxygen 8—one proportion.

Hence a number of laws may be deduced which must hold in every sulphate of a protoxide.

1. The oxygen of the acid is a multiple of that of the base.
2. The acid contains three times as much oxygen as the base.
3. The sulphur of the acid is just double the oxygen of the base.
4. The acid itself is five times as much as the oxygen of the base.

Metallic sulphurets are frequently composed of one proportion of each element; and should oxidation ensue, so that the sulphur is converted into sulphuric acid, and the metal into a protoxide, they will be in the exact proportion for forming a neutral sulphate. Berzelius

has proved by analysis that this happens frequently, and he is disposed to convert it into a general law.

Again, the carbonates are composed of one proportion of carbonic acid, and one proportion of some protoxide. But one proportion of carbonic acid is composed of

Carbon 6, one proportion.
Oxygen 16, two proportions.

and every protoxide of

Metal one proportion.
Oxygen 8, one proportion.

It is inferred, therefore, that in all the carbonates, the oxygen of the acid is exactly double that of the base; and the same mode of reasoning is applicable to the various genera of salts. These few examples will suffice to show, that what seemed so obsure to Berzelius, is rendered quite obvious by the Daltonian method. We perceive, moreover, that no constant ratio can exist between the quantity of oxide and that of the acid or oxygen of the acid; and the reason is, because the atomic weights of the metals in general are different. But this view of the subject answers another useful purpose; it enables us to see whether the law of Berzelius is or is not universal. The observations made on this subject by Dr. Thomson, in his "First Principles of Chemistry," are so much to the point, that I cannot do better than give them in his own words.

"Before concluding these general observations," says Dr Thomson, "I may say a few words on Berzelius' law, that in all salts, the atoms of oxygen in the acid constitute a multiple by a whole number of the atoms of oxygen of the base. This law was founded upon the first set of exact analyses of neutral salts which Berzelius made. Now, as neutral salts in general are combinations of an atom of a protoxide with an atom of an acid, it is obvious that the atoms of oxygen in the acid must in all such salts be multiples of the atom of oxygen in the base; because every whole number is a multiple of unity. Neutral salts, therefore, are not the kind of salts by means of which the precision of this supposed law can be put to the test.

"Even in the subsalts, composed of 1 atom of acid united to 2 atoms of base, it is obvious enough that the law will hold whenever the acid combined with the base happens to contain 2 or 4, or any even number of atoms; because all even numbers are multiples of 2. Now this is the case with the following acids:

| | | | |
|---|---|---|---|
| Phosphoric. | Nitrous. | Antimonic. | Citric. |
| Carbonic. | Titanic | Manganesic. | Saclactic |
| Boracic. | Arsenious. | Molybdous. | Chromous. |
| Sulphurous. | Selenic. | Uranitic. | |

Consequently, the law must hold good in all combinations of 1 atom of these acids with 2 atoms of base."

"In the case of all those acids which contain only one atom of oxygen, all the subsalts composed of 1 atom of the acid united to 2 atoms of base, the law will also in some sort hold: for the atoms of the oxygen in such acids being 1, this number will always be a submultiple of 2, the number of atoms of oxygen in 2 atoms of base. This is the case with the following acids:

| | |
|---|---|
| Silicic | Hypo-sulphurous. |
| Phosphorous. | Oxide of tellurium. |

"It is only in the subsalts of acids containing an odd number of atoms of oxygen, that exceptions to the law can exist. It is to them, therefore, that we must have recourse when we wish to determine whether this empirical law of Berzelius be founded in nature or not. Now, there are 13 acids, the integrant particles of which contain an odd number of atoms of oxygen. The following table exhibits the names of these acids, together with the number of atoms of oxygen in each.

| | *Atoms of Oxygen.* | | *Atoms of Oxygen.* |
|---|---|---|---|
| " Sulphuric acid . . | 3 | Acetic acid . . | 3 |
| Arsenic . . . | 3 | Succinic . . . | 3 |
| Chromic . . . | 3 | Benzoic . . | 3 |
| Molybdic . . . | 3 | Nitric . . . | 5 |
| Tungstic . . . | 3 | Tartaric . . . | 5 |
| Oxalic . . . | 3 | Hypo-sulphuric . | 2½" |
| Formic . . . | 3 | | |

Dr Thomson informs us that the number of subsalts he has examined is exceedingly small, because his "object was not to investigate the truth of Berzelius' law, but to determine the quantity of water of crystallization which the salts contain." He observes, that "it would certainly be a most remarkable circumstance, if 2 atoms of any protoxide were incapable of combining with 1 atom of any of the 13 acids in the preceding list." Dr T. adduces seven instances in which this does happen, three of which are completely in point, being a subsulphate of alumina, a subacetate of lead, and a subacetate of copper; and he is "persuaded that many more will be discovered whenever the attention of chemists is particularly turned to the subsalts." He also mentions other kinds of salts, in regard to which, for equally obvious reasons, the law cannot and does not hold.

These extracts will suffice for placing the law of Berzelius in its true light; for showing that it is a direct consequence of the general operation of the Laws of Definite Proportion; and that we must expect to find some exceptions to his law, derived from the very cause which gives rise to it. It is to be hoped that Berzelius will take the remarks of Dr Thomson into mature consideration, by which he will probably perceive that his favourite canon is not so universal as he imagines, and be led to avoid the errors to which, from its indiscriminate employment, both himself and his pupils might otherwise be exposed.

That part of the law which applies to the combined water is likewise more than doubtful. When the base contains 2 equivalents of oxygen and an uneven number of equivalents of water is present, it cannot be correct. When the base contains 3 equivalents of oxygen, the law would not apply whenever there chanced to be 2, 4, 8, or 10 equivalents of water. When the base has only one equivalent of oxygen, then it must hold for obvious reasons. If the base has an equivalent and a half of oxygen, the law can only be true when 3, 6, 9, or 12 equivalents of water are in combination; with 1, 2, 4, 5, 7, 8, or 10, it must fail.

An attempt has been made within these few years to determine the atomic constitution of minerals, an inquiry in which Berzelius has highly distinguished himself. The composition of minerals must of course be influenced by the usual laws of combination, though there are sometimes obstacles in the way of discovering it. In the compounds made artificially, chemists possess the power of having each constituent perfectly pure; but, unfortunately, we cannot always com-

mand the same condition with respect to natural productions. The materials of which a mineral is composed, once formed part of some heterogeneous fluid or semi-fluid mass, and in assuming the solid form are very likely to have enclosed within them some substance which is not, chemically considered, an essential ingredient of the mineral. The result of chemical analysis, accordingly, does not always give us a view of the actual constitution of a mineral species; some substances are often detected which are foreign to it, and the chemist must exercise his judgment in determining what is and what is not essential. Now nothing is so well calculated to direct him as a knowledge of the laws of combination; but as a great discretionary power is in his hands, it is important that his mode of investigation should be the simplest possible, and that his rules should be founded on well-established principles, which involve nothing hypothetical. It is but very lately that due care has been bestowed in selecting sufficiently pure specimens for examination, or in performing the analyses themselves with the precision necessary for determining the chemical constitution of minerals. It were much to be wished, that the first essays in this difficult field should be confined as much as possible to such minerals as contain but few substances, and which occur in distinct transparent crystals.

We are indebted to Berzelius for this mode of studying the composition of minerals; and certainly if skill in analytical investigation could encourage any one to make the attempt, none could undertake it with greater chance of success than the indefatigable Professor of Stockholm. Unfortunately his theoretical views are unnecessarily complex, and I much doubt, for reasons already stated, if his ruling law about multiples of oxygen deserves the confidence he bestows upon it. It will not, I am convinced, be adopted by the chemists and mineralogists of this country, and I am much mistaken if, notwithstanding the great reputation of its author, it stand its ground long upon the continent. To give a particular description of his method is foreign to my purpose, but the reader will find an able account of it in the 9th vol. of the Annals of Philosophy, N. S. by Mr Children.

## SECTION III.

### *OXYGEN.*

Oxygen gas was discovered by Priestley in 1774, and by Scheele a year or two after, without previous knowledge of Priestley's discovery. Several appellations have been given to it. Priestley named it *Dephlogisticated air*; it was called *Empyreal air* by Scheele, and *Vital air* by Condorcet. The name it now bears, derived from the Greek words ὀξὺς *acid* and γεννάω I *generate*, was proposed by Lavoisier, from the supposition that it is the sole cause of acidity.

Oxygen gas may be obtained from several sources. The peroxides of manganese, lead, and mercury, nitre, and the chlorate of potassa, all yield it in large quantity when they are exposed to a red heat. The substances commonly employed for the purpose are the peroxide of manganese and the chlorate of potassa. It may be procured from the former in two ways; either by heating it to redness in a gun-barrel, or in a retort of iron or earthen-ware; or by putting it into a flask with half its weight of concentrated sulphuric acid, and heating the mixture

by means of a lamp. To understand the theory of these processes, it is necessary to be aware that there are three distinct oxides of manganese, which are thus constituted:

| | *Manganese.* | *Oxygen.* | |
|---|---|---|---|
| Protoxide | 28, or one prop. | + 8 | =36 |
| Deutoxide | 28 | +12 | =40 |
| Peroxide | 28 | +16 | =44 |

On applying a red heat to the last, it parts with half a proportion of oxygen, and is converted into the deutoxide. Every 44 grains of the peroxide will therefore lose, if quite pure, 4 grains of oxygen, or nearly 12 cubic inches; and one ounce will yield about 128 cubic inches of gas. The action of sulphuric acid is different. The peroxide loses a whole proportion of oxygen, and is converted into the protoxide, which unites with the acid, forming a sulphate of the protoxide of manganese. Every 44 grains of the peroxide must consequently yield 8 grains of oxygen and 36 of the protoxide, which, by uniting with one proportion (40) of the acid, forms 76 of the sulphate. The first of these processes is the most convenient in practice.

The gas obtained from the peroxide of manganese, though hardly ever quite pure, owing to the presence of iron, carbonate of lime, and other earthy substances, is sufficiently good for ordinary purposes. It yields a gas of better quality, if previously freed from the carbonate of lime by dilute muriatic or nitric acid; but when oxygen of great purity is required, it is better to obtain it from the chlorate of potassa. For this purpose, the salt should be put into a retort of green glass, or of white glass made without lead, and be heated nearly to redness. It first becomes liquid, though quite free from water, and then, on increase of heat, is wholly resolved into pure oxygen gas, which escapes with effervescence, and into a white compound, called the chloride of potassium, which is left in the retort. The theory of the decomposition is as follows. The chlorate of potassa is composed of

Chloric acid 76, or one proportion.
Potassa 48, or one proportion.

124

Chloric acid consists of

Chlorine 36, or one proportion.
Oxygen 40, or five proportions.

76

and potassa of

Potassium 40, or one proportion.
Oxygen 8, or one proportion.

48

The chlorine and potassium are both deprived of their oxygen, and then unite together. So that 124 grains of the salt are resolved into 76 grains of the chloride of potassium, and 48 grains, or 141 cubic inches, of pure oxygen.

Oxygen gas is colourless, has neither taste nor smell, is not chemically affected by the imponderables, refracts light very feebly, and is a non-conductor of electricity. It is the most perfect negative electric

that we possess, always appearing at the positive pole, when any compound which contains it is exposed to the action of galvanism. It emits light, as well as heat, when suddenly and forcibly compressed.

Oxygen is heavier than atmospheric air. Chemists have differed as to its precise weight; but the late experiments of Dr Thomson, (First Principles of Chemistry,) leave little doubt of the accuracy of Dr Prout's estimate as stated in the 6th volume, O. S., of the Annals of Philosophy. According to that chemist, 100 cubic inches of oxygen, when the thermometer is at 60° F, and the barometer stands at 30 inches, weigh 33.888 grains, and its specific gravity must be 1.1111.

Oxygen gas is very sparingly absorbed by water, 100 cubic inches of that liquid dissolving only three or four of the gas. It has neither acid nor alkaline properties, for it does not redden or turn green the blue vegetable colours, nor does it evince a disposition to unite directly either with acids or alkalies. It has a very powerful attraction for most of the simple bodies; and there is not one of them with which it may not be made to combine. The act of combining with oxygen is called *oxidation*, and the bodies, after having united with it, are said to be *oxidized*. The compounds so formed are divided by chemists into acids and oxides. The first division includes those compounds which possess the general properties of acids; and the second comprehends those which not only want that character, but many of which are highly alkaline, and yield salts by uniting with acids. The phenomena of oxidation are variable. It is sometimes produced with great rapidity, and with evolution of heat and light. Ordinary combustion, for instance, is nothing more than rapid oxidation; and all inflammable or combustible substances derived their power of burning in the open air from their affinity for oxygen. On other occasions it takes place slowly, and without any appearance either of heat or light, as is exemplified by the rusting of iron when exposed to a moist atmosphere. Different as these processes may appear, oxidation is the result of both; and both are owing to the same circumstance, namely, to the presence of oxygen in the atmosphere.

All substances that are capable of burning in the open air, burn with far greater brilliancy in oxygen gas. A piece of wood on which the least spark of light is visible, bursts into flame the moment it is put into a jar of oxygen; lighted charcoal emits beautiful scintillations; and phosphorus burns with so powerful and dazzling a light that the eye cannot bear its impression. Even iron and steel, which are not commonly ranked among the inflammables, undergo a rapid combustion in oxygen gas.

The changes that accompany these phenomena are no less remarkable than the phenomena themselves. When a lighted taper is put into a vessel of oxygen gas, it burns for a while with increased splendour; but the size of the flame soon begins to diminish, and if the mouth of the jar be properly secured by a cork, the light will in a short time disappear entirely. The gas has now lost its characteristic property; for a second lighted taper, immersed in it, is instantly extinguished. This result is general. The burning of one body in a given portion of oxygen unfits it more or less completely for supporting the combustion of another; and the reason is manifest. Combustion is produced by the combination of inflammable matter with oxygen gas. The quantity of free oxygen, therefore, diminishes during the process, and is at length nearly or quite exhausted. The burning of all bodies, however inflammable, must then cease, because the presence of oxygen is necessary to its continuance. For this reason oxygen gas is called a supporter of combustion. The oxygen often loses its gaseous

form as well as its other properties. If phosphorus or iron be burned in a jar of pure oxygen over water or mercury, the disappearance of the gas becomes obvious by the ascent of the liquid, which is forced up by the pressure of the atmosphere, and fills the vessel. Sometimes, on the contrary, the oxygen suffers only a partial diminution of volume, or even undergoes no change of bulk at all, as is exemplified by the combustion of the diamond.

The changes experienced by the burning body are equally striking. While the oxygen loses its power of supporting combustion, the inflammable substance lays aside its combustibility. It is now an oxidized body, and cannot be made to burn even by aid of the purest oxygen. It has also acquired an addition to its weight. It is an error to suppose that bodies lose any thing while they burn. The materials of our fires and candles do indeed disappear, but they are not destroyed. Although they fly off in the gaseous form, and are commonly lost to us, it is not difficult to collect and preserve all the products of combustion. When this is done with the requisite care, it is constantly found that the combustible matter weighs more after than before combustion; and that the increase in weight is exactly equal to the quantity of oxygen which has disappeared during the process.

Oxygen gas is necessary to respiration. No animal can live in an atmosphere which does not contain a certain portion of uncombined oxygen; for an animal soon dies if put into a portion of air from which the oxygen has been previously removed by a burning body. It may therefore be anticipated that oxygen is consumed during respiration. If a bird be confined in a limited quantity of atmospheric air, it will at first feel no inconvenience; but as a portion of oxygen is withdrawn at each inspiration, its quantity diminishes rapidly, so that respiration soon becomes laborious, and in a short time ceases altogether. Should another bird be then introduced into the same air, it will die in the course of a few seconds; or if a lighted candle be immersed in it, its flame will be extinguished. Respiration and combustion have therefore the same effect. An animal cannot live in an atmosphere which is unable to support combustion; nor can a candle burn in air which contains too little oxygen for respiration.

## *On the Theory of Combustion.*

The only phenomena of combustion noticed by an ordinary observer, are the destruction of the burning body, and the development of heat and light; but it has been demonstrated that, in addition to these circumstances, oxygen gas invariably disappears, and a new compound, consisting of oxygen and the combustible is generated. The term *combustion*, therefore, in its common signification, implies the rapid union of oxygen gas and combustible matter, accompanied with heat and light. As the evolution of heat and light is dependent on chemical action, the same phenomena may be expected in other chemical processes; and accordingly heat and light are frequently emitted quite independently of oxygen. Thus phosphorus takes fire, and a taper burns for a short time, in a vessel of chlorine; and several of the common metals, such as copper, antimony, and arsenic, in a state of fine division, become red-hot when introduced into a jar of that gas. Potassium takes fire in cyanogen gas, and copper leaf or iron wire, if moderately heated, undergoes the same change in the vapour of sulphur. A mixture of iron filings and sulphur, when heated so as to bring the latter into perfect fusion, emits intense heat and light at the instant of combination; and a like effect, though in a far less degree, is produced

by the action of concentrated sulphuric acid on pure magnesia. Most of these and similar examples, especially when one of the combining substances is gaseous, are frequently included under the idea of combustion; and they certainly belong to the same class of phenomena. In the subsequent observations, however, I shall employ the term in its ordinary sense; but the remarks concerning increase of temperature, whether with or without light, apply equally to all cases where heat is developed as a result of chemical action.

For many years prior to the discovery of oxygen gas, the phenomena of combustion were explained on the Stahlian or phlogistic hypothesis. All combustible bodies, according to Stahl, contain a certain principle which he called *phlogiston*, to the presence of which he ascribed their combustibility. He supposed that when a body burns, phlogiston escapes from it; and that when the body has lost phlogiston, it ceases to be combustible, and is then a dephlogisticated or incombustible substance. A metallic oxide was consequently regarded as a simple substance, and the metal itself as a compound of its oxide with phlogiston. The heat and light which accompany combustion were attributed to the rapidity with which phlogiston is evolved during the process.

The discovery of oxygen proved fatal to the Stahlian doctrine. Lavoisier had the honour of overthrowing it, and of substituting in its place the antiphlogistic theory. The basis of his doctrine has already been stated;—that combustion and oxidation in general consist in the combination of the combustible material with oxygen. This fact he established beyond a doubt. On burning phosphorus in a jar of oxygen, he observed that a considerable quantity of the gas disappeared; that the phosphorus gained materially in weight, and that the increase of the latter exactly corresponded to the loss of the former. An iron wire was burnt in a similar manner, and the weight of the oxidized iron was found equal to that of the wire originally employed, added to the quantity of oxygen which had disappeared. That the oxygen is really present in the oxidized body he proved by a very decisive experiment. Some liquid mercury was confined in a vessel of oxygen gas, and exposed to a temperature sufficient for causing its oxidation. The oxide of mercury, so produced, was put into a small retort and heated to redness, when it was reconverted into oxygen and fluid mercury, the quantity of the oxygen being exactly equal to what had combined with the mercury in the first part of the operation.

To account for the production of heat and light during combustion, Lavoisier had recourse to Dr Black's Theory of latent caloric. Heat is always evolved, whenever a substance, without change of form, passes from a rarer into a denser state, and also when a gas becomes liquid or solid, or a liquid solidifies; because a quantity of caloric previously combined, or latent within it, is then set free. Now this is precisely what happens in many instances of combustion. Thus water is formed by the burning of hydrogen, in which case two gases give rise to a liquid; and in forming phosphoric acid with phosphorus, or in oxidizing the metals, oxygen is condensed into a solid. When the product of combustion is gaseous, as in the burning of charcoal, the evolution of heat is ascribed to the circumstance that the oxidized body contains a less quantity of combined caloric, or has a less specific caloric, than the substances by which it is produced.

This is the weak point of Lavoisier's theory. Chemical action is very often accompanied by increase of temperature, and the caloric evolved during combustion is only a particular instance of it. Any theory, therefore, by which it is proposed to account for the production of heat in some cases, ought to be applicable to all. When com-

bustion, or any other chemical action is followed by considerable condensation, in consequence of which the new body contains less insensible caloric than its elements did before combination, it is obvious that heat will, in that case, be disengaged. But if this is the sole cause of the phenomenon, it follows that a rise of temperature ought always to be preceded by a corresponding diminution of capacity for caloric, and that the extent of the former ought to be in a constant ratio with the degree of the latter. Now Petit and Dulong infer from their researches on this subject, (Annales de Chim. et de Phys. vol x.) that the degree of heat developed during combination, bears no relation to the specific caloric of the combining substances; and that in the majority of cases, the evolution of heat is not attended by any diminution in the capacity of the compound. It is a well known fact, that increase of temperature frequently attends chemical action, though the products contain much more insensible caloric than the substances from which they are formed. This happens remarkably in the explosion of gunpowder, which is attended by intense heat; and yet its materials, in passing from the solid to the gaseous state, expand to at least 250 times their volume, and consequently render latent a large quantity of caloric.

These circumstances leave no doubt that the evolution of caloric during chemical action is owing to some cause quite unconnected with that assigned by Lavoisier; and if this cause operates so powerfully in some cases, it is fair to infer that part of the effect must be owing to it on those occasions, when the phenomena appear to depend on change of capacity alone. A new theory is therefore required to account for the chemical production of heat. But it is easier to perceive the fallacies of one doctrine, than to substitute another which shall be faultless; and it appears to me that chemists must, for the present, be satisfied with the simple statement, that energetic chemical action does of itself give rise to increase of temperature. Berzelius, in adopting the electro-chemical theory, regards the heat of combination as an electrical phenomenon; and he believes it to arise from the oppositely electrical substances neutralizing one another, in the same manner as the electric equilibrium is restored during the discharge of a Leyden phial. But such an opinion can only be held by those who adopt the electro-chemical theory; and even admitting the accuracy of this doctrine, the reasoning founded on it by Berzelius appears to me inadmissible. For, according to the theory, the two elements of a compound retain their peculiar state of excitement. This condition is essential to the continuance of the union, and therefore the act of combination is not analogous to the discharge of a Leyden phial. The equilibrium is restored in one case, but not in the other.

The caloric emitted during combustion varies with the nature of the material. The effect of the combustible gases in raising the temperature of water, according to the experiments of Mr Dalton, is shown in the following table. (Chemical Philosophy, II. 309.)

| | |
|---|---|
| Hydrogen, in burning, raises an equal volume of water . | 5° F. |
| Carbonic oxide . . . . . . . . . . . | $4\frac{1}{2}$ |
| Light carburetted hydrogen . . . . . . . | 18 |
| Olefiant gas . . . . . . . . . . . | 27 |
| Coal gas, varies with the quality of the gas from 10 to . | 16 |
| Oil gas, varies also with the quality of the gas from 12 to . | 20 |

Mr Dalton further states that generally the combustible gases give out heat nearly in proportion to the oxygen which they consume.

In the thirty-seventh volume of the An. de Ch. et Ph. page 189, M. Despretz has given a notice of some experiments on the heat developed in combustion. The substances burned were hydrogen. carbon, phosphorus, and several metals, and so much of each was employed, as to require the same quantity of oxygen. When the combustion of hydrogen gas produced 2578 degrees of heat, carbon gave out 2967, and iron 5325. Phosphorus, zinc, and tin, emit quantities of caloric very nearly the same as iron. Hence it follows that, for equal quantities of oxygen, hydrogen in burning evolves less heat than most other substances. These results do not accord with those of Mr Dalton.

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## SECTION IV.

### *HYDROGEN.*

This gas was formerly termed *inflammable* air from its combustibility, and *phlogiston* from the supposition that it was the matter of heat; but the name *hydrogen*, derived from *ὕδωρ water*, has now become general. Its nature and leading properties were first pointed out in the year 1766 by Mr Cavendish. (Philos. Trans. LVI. 144.)

Hydrogen gas may be easily procured in two ways. The first consists in passing the vapour of water over metallic iron heated to redness. This is done by putting iron wire into a gun-barrel open at both ends, to one of which is attached a retort containing pure water, and to the other a bent tube. The gun-barrel is placed in a furnace, and when it has acquired a full red heat, the water in the retort is made to boil briskly. The gas, which is copiously disengaged as soon as the steam comes in contact with the glowing iron, passes along the bent tube, and may be collected in convenient vessels, by dipping the free extremity of the tube into the water of a pneumatic trough*. The second and most convenient method consists in putting pieces of iron or zinc into dilute sulphuric acid, formed of one part of strong acid to four or five of water. Zinc is generally preferred. The hydrogen obtained in these processes is not absolutely pure. The gas evolved during the solution of iron has an offensive odour, ascribed by Berzelius to the presence of a volatile oil, which may be almost entirely removed by transmitting the gas through alcohol. The oil appears to arise from some compound being formed between hydrogen and the carbon which is always contained even in the purest kinds of common iron; and it is probable that a little carburetted hydrogen-gas is generated at the same time. The zinc of commerce contains sulphur, and almost always traces of charcoal, in consequence of which it is contaminated with sulphuretted hydrogen, and probably with the same impurities, though in a less degree, as are derived from iron. A little metallic zinc is also contained in it, apparently in combination with hydrogen. All these impurities, carburetted hydrogen excepted, may be removed by passing the hydrogen through a solution of pure potassa. To obtain hydrogen of great purity, distilled zinc should be employed.

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* The mode of collecting gases, together with the apparatus employed for that purpose, will be described in the fourth part of this work.

Hydrogen is a colourless gas, and has neither odour nor taste when perfectly pure. It is a powerful refractor of light. Like oxygen, it cannot be resolved into more simple parts, and like that gas, has hitherto resisted all attempts to compress it into a liquid. It is the lightest body in nature, and is consequently the best material for filling balloons. From its extreme lightness it is difficult to ascertain its precise density by weighing, because the presence of minute quantities of common air or watery vapour occasions considerable error. From the composition of water, hydrogen gas is inferred to be sixteen times lighter than oxygen; and the weight of 100 cubic inches at 60° and thirty inches of the barometer, should therefore be $\frac{33.888}{16}$, or 2.118 grains. Its specific gravity is consequently 0.0694, as stated some years ago by Dr Prout.

Hydrogen does not change the blue colour of vegetables. It is sparingly absorbed by water, 100 cubic inches of that liquid dissolving about one and a half of the gas. It cannot support respiration; for an animal soon perishes when confined in it. Death ensues from deprivation of oxygen rather than from any noxious quality of the hydrogen; since an atmosphere composed of a due proportion of oxygen and hydrogen gases may be respired without inconvenience. Nor is it a supporter of combustion; for when a lighted candle fixed on wire is passed up into an inverted jar full of hydrogen, the light disappears on the instant.

Hydrogen gas is inflammable in an eminent degree; though, like other combustibles, it requires the aid of a supporter for enabling its combustion to take place. This is exemplified by the experiment above alluded to, in which the gas is kindled by the flame of the candle, but burns only where it is in contact with the air. Its combustion, when conducted in this manner, goes on tranquilly, and is attended with a yellowish-blue flame and a very feeble light. The phenomena are different when the hydrogen is previously mixed with a due quantity of atmospheric air. The approach of flame not only sets fire to the gas near it, but the whole is kindled at the same instant; a flash of light passes through the mixture, followed by a violent explosion. The best proportion for the experiment is two measures of hydrogen, to five or six of air. The explosion is far more violent when pure oxygen is used instead of atmospheric air, particularly when the gases are mixed together in the ratio of one measure of oxygen to two of hydrogen.

Oxygen and hydrogen gases cannot combine at ordinary temperatures, and may, therefore, be kept in a state of mixture without even gradual combination taking place between them. Hydrogen may be set on fire, when in contact with air or oxygen gas, by flame, by a solid body heated to bright redness, and by the electric spark. If a jet of hydrogen be thrown upon recently prepared spongy platinum, this metal almost instantly becomes red-hot, and then sets fire to the gas, a discovery which was made in the year 1824 by Professor Doebereiner of Jena. The power of flame and electricity in causing a mixture of hydrogen with air or oxygen gas to explode, is limited. Mr Cavendish found that flame occasions a very feeble explosion when the hydrogen is mixed with nine times its bulk of air; and that a mixture of four measures of hydrogen to one of air does not explode at all. An explosive mixture formed of two measures of hydrogen to one of oxygen, explodes from all the causes above enumerated. M. Biot found that sudden and violent compression likewise causes an explosion, apparently from the heat emitted during the operation; for an

equal degree of condensation, slowly produced, has not the same effect. The electric spark ceases to cause detonation when the explosive mixture is diluted with twelve times its volume of air, fourteen of oxygen, or nine of hydrogen, or when it is expanded to sixteen times its bulk by diminished pressure. I find that spongy platinum acts just as rapidly as flame or the electric spark in producing explosion, provided the gases are quite pure and mixed in the exact ratio of two to one*.

When the action of heat, the electric spark, and spongy platinum no longer cause an explosion, a silent and gradual combination between the gases may still be occasioned by them. Sir H. Davy observed that oxygen and hydrogen gases unite slowly with one another, when they are exposed to a temperature above the boiling point of mercury, and below that at which glass begins to appear luminous in the dark. An explosive mixture diluted with air to too great a degree to explode by electricity, is made to unite silently by a succession of electric sparks. Spongy platinum causes them to unite slowly, though mixed with one hundred times their bulk of oxygen gas.

A large quantity of caloric is evolved during the combustion of hydrogen gas. Lavoisier concludes from experiments made with his calorimeter, (Elements, vol. i.) that one pound of hydrogen occasions so much heat in burning as is sufficient to melt 295.6 pounds of ice. Mr Dalton fixes the quantity of ice at 320 pounds, and Dr Crawford at 480. The most intense heat that can be produced, is caused by the combustion of hydrogen in oxygen gas. Dr Hare of Philadelphia, who first burned hydrogen for this purpose, collected the gases in separate gas-holders, from which a stream was made to issue through tubes communicating with one another, just before their termination. At this point the jet of the mixed gases was inflamed. The effect of the combustion, though very great, is materially increased by forcing the two gases in due proportion into a strong metallic vessel by means of a condensing syringe, and setting fire to a jet of the mixture as it issues. An apparatus of this kind, now known by the name of the oxy-hydrogen blowpipe, was contrived by Mr Newman, and employed by the late Professor Clarke in his experiments on the fusion of refractory substances. On opening a stopcock which confines the compressed gases, a jet of the explosive mixture issues with force through a small blowpipe tube, at the extremity of which it is kindled. In this state, however, the apparatus should never be used; for as the reservoir is itself full of an explosive mixture, there is great danger of the flame running back along the tube, and setting fire to the whole gas at once. To prevent the occurrence of such an accident, which would most probably prove fatal to the operator, Professor Cumming proposed that the gas, as it issues from the reservoir, should be made to pass through a cylinder full of oil or water, before reaching the point at which it is to burn; and Dr Wollaston suggested the additional precaution of fixing successive layers of fine wire gauze within the exit tube, each of which would be capable of intercepting the communication of flame. But this apparatus is rarely necessary in chemical researches. A very intense heat, quite sufficient for most purposes, may be safely and

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* For a variety of facts respecting the causes which prevent the action of flame, electricity, and platinum in producing detonation, the reader may consult the Essay of M. Grotthus in the Ann. de Chimie, vol. lxxxii.; Sir H. Davy's work on flame; Dr Henry's Essay in the Philosophical Transactions for 1824; and a paper by myself in the Edinburgh Philosophical Journal for the same year.

easily procured by passing a jet of oxygen gas through the flame of a spirit lamp, as proposed by the late Dr Marcet.

Water is the sole product of the combustion of hydrogen gas. For this important fact we are indebted to Mr Cavendish. He demonstrated it by burning oxygen and hydrogen gases in a dry glass vessel, when a quantity of pure water was generated exactly equal in weight to that of the gases which had disappeared. This experiment, which is the synthetic proof of the composition of water, was afterwards made on a much larger scale in Paris by Vauquelin, Fourcroy, and Seguin. Laveisier first demonstrated its nature analytically, by passing a known quantity of watery vapour over metallic iron heated to redness in a glass tube. Hydrogen gas was disengaged, the metal in the tube was oxidized, and the weight of the former, added to the increase which the iron had experienced from combining with oxygen, exactly corresponded to the quantity of water which had been decomposed.

It will soon appear that a knowledge of the exact proportions in which oxygen and hydrogen gases unite to form water, is a necessary element in many chemical reasonings. Its composition by volume was demonstrated very satisfactorily by Messrs Nicholson and Carlisle, in their researches on the chemical agency of galvanism. On resolving water into its elements by this agent, and collecting them in separate vessels, they obtained precisely two measures of hydrogen to one of oxygen,—a result which has been fully confirmed by subsequent experimenters. The same fact was proved synthetically by Gay-Lussac and Humboldt, in their Essay on Eudiometry, published in the *Journal de Physique* for 1805. They found that when a mixture of oxygen and hydrogen is inflamed by the electric spark, those gases always unite in the exact ratio of one to two, whatever may be their relative quantity in the mixture. When one measure of oxygen is mixed with three of hydrogen, one measure of hydrogen is the residue after the explosion; and a mixture of two measures of oxygen and two of hydrogen leaves one measure of oxygen. When one volume of oxygen is mixed with two of hydrogen, both gases, if quite pure, disappear entirely on the electric spark being passed through them. The composition of water by weight was determined with great care by Berzelius and Dulong; and we cannot hesitate, considering the known dexterity of the operators, and the principle on which their method of analysis was founded, to regard their result as a nearer approximation to the truth than that of any of their predecessors. They state as a mean of three careful experiments, (Ann. de Ch. et de Ph. vol. xv.) that 100 parts of pure water consist of 88.9 of oxygen and 11.1 of hydrogen. Now,

$$11.1 : 88.9 :: 1 : 8.009$$

which is so near the proportion of 1 to 8 as to justify the adoption of that ratio. Hence, the constitution of water by weight and measure, may be thus stated:

| | *By Weight.* | *By Volume.* |
|---|---|---|
| Oxygen . | 8 . . | 1 |
| Hydrogen . | 1 . . | 2 |

These are the data from which it was inferred that oxygen gas is just 16 times heavier than hydrogen. The atomic weights of oxygen and hydrogen are deduced from the same analysis. As no compound of these substances is known which has a less proportion of oxygen than water, it is supposed to contain one atom of each of its constituents. This view of the atomic constitution of water appears to be justified by

the strong affinity which its elements evince for one another, as well as from the proportions with which they respectively combine with other bodies. Consequently, regarding the atom of hydrogen as unity, 8 will be the relative weight of an atom of oxygen.

The processes for procuring a supply of hydrogen gas will now be intelligible. The first is the method by which Lavoisier made the analysis of water. It is founded on the fact that iron at a red heat decomposes water, the oxygen of that liquid uniting with the metal, and the hydrogen gas being set free. That the hydrogen which is evolved when the zinc or iron is put into dilute sulphuric acid must be derived from the same source, is obvious from the consideration that of the three substances, iron, sulphuric acid, and water, the last is the only one which contains hydrogen. The product of the operation, besides hydrogen, is the sulphate of the protoxide of iron, if iron is used, or of the oxide of zinc, when zinc is employed. The knowledge of the combining proportions of these substances will readily give the exact quantity of each product. These numbers are,

| | |
|---|---|
| Water (8 oxy. +1 hyd.) . . . | 9 |
| Sulphuric acid . . . . | 40 |
| Iron . . . . . | 28 |
| Ptotoxide of iron (28 iron +8 oxygen) | 36 |
| Sulphate of the protoxide of iron (40+36) | 76 |

Hence for every 9 grains of water which are decomposed, 1 grain of hydrogen will be set free; 8 grains of oxygen will unite with 28 grains of iron, forming 36 of the protoxide of iron; and the 36 grains of the protoxide will combine with 40 grains of sulphuric acid, yielding 76 of the sulphate of the protoxide of iron. A similar calculation may be employed when zinc is used, merely by substituting the atomic weight of zinc (34) for that of iron.—According to Mr Cavendish, an ounce of zinc yields 676 cubic inches, and an equal quantity of iron 782 cubic inches of hydrogen gas.

The action of diluted sulphuric acid on metallic zinc affords an instance of what was once called *Disposing Affinity*. Zinc cannot decompose water at common temperatures; but as soon as sulphuric acid is added, the decomposition of the water takes place rapidly, though the acid merely unites with the oxide of zinc. The former explanation was, that the affinity of the acid for the oxide of zinc disposed the metal to unite with the oxygen, and thus enabled it to decompose water; that is, the oxide of zinc was supposed to produce an effect previous to its existence. The obscurity of this explanation arises from regarding changes as consecutive, which are in reality simultaneous. There is no appearance of succession in the process; the oxide of zinc is not formed previously to its combination with the acid, but at the same instant. There is, as it were, only one chemical change, which consists in the combination, at one and the same moment, of the zinc with the oxygen, and the oxide of zinc with the acid; and this change occurs because these two affinities, acting together, overcome the attraction of oxygen and hydrogen for one another.

Water is a transparent colourless liquid, which has neither smell nor taste. It is a powerful refractor of light, conducts heat very slowly, and is an imperfect conductor of electricity. It is compressible by very strong pressure. The fact was long disputed; but Mr Perkins finds that the pressure of 2000 atmospheres occasions a diminution of 1-12th of its bulk. According to the experiments of Professor Oersted, this estimate is far too great. (Edin. Journal of Science, No. XII. p. 201.) The relations of water, with respect to caloric, are highly important,

but have already been discussed in the first part of the work. The specific gravity of water is 1, the density of all solid and liquid bodies being referred to it as a term of comparison. One cubic inch at 60° F. and 30 Bar., weighs 252.525 grains, so that it is 828 times heavier than atmospheric air.

Water is one of the most powerful chemical agents which we possess. Its agency is owing partly to the extensive range of its own affinity, and partly to the nature of its elements. The effect of the last circumstance has already appeared in the process for procuring hydrogen gas; and indeed there are few complex chemical changes which do not give rise either to the production or decomposition of water. But, independently of the elements of which it is composed, it combines directly with many bodies. Sometimes it is contained in a variable ratio, as in ordinary solution; in other compounds it is present in a fixed definite proportion, as is exemplified by its union with several of the acids, the alkalies, and all salts that contain water of crystallization. These combinations are termed *hydrates*; thus, concentrated sulphuric acid is a compound of one equivalent of the real dry acid and one equivalent of water; and its proper name is *hydrous sulphuric acid*, or *hydrate of sulphuric acid*. The adjunct *hydro* has been sometimes used to signify the presence of water in definite proportion; but it is advisable, to prevent mistakes, to limit its employment to the compounds of hydrogen.

The purest water which can be found as a natural product, is procured by melting freshly fallen snow, or by receiving rain in clean vessels at a distance from houses. But this water is not absolutely pure; for if placed under the exhausted receiver of an air-pump, or boiled briskly for a few minutes, bubbles of gas escape from it. The air obtained in this way from snow water, is much richer in oxygen gas than atmospheric air. According to the experiments of Gay-Lussac and Humboldt, it contains 34.8 per cent of oxygen, and the air separated by ebullition from rain-water contains 32 per cent of that gas. All water which has once fallen on the ground, becomes impregnated with more or less earthy or saline matters, and it can be separated from them only by distillation. The distilled water, thus obtained, and preserved in clean well-stopped bottles, is absolutely pure. Recently boiled water has the property of absorbing a portion of all gases, when its surface is in contact with them; and the absorption is promoted by brisk agitation. The following table, from Dr Henry's Chemistry, shows the absorbability of different gases by water, deprived of all its air by ebullition.

100 cubic inches of such water, at the mean temperature and pressure, absorb of

| | *Dalton and Henry.* | *Saussure.* |
|---|---|---|
| Sulphuretted Hydrogen | 100 cubic in. | 253 |
| Carbonic Acid | 100 | 106 |
| Nitrous Oxide | 100 | 76 |
| Olefiant Gas | 12.5 | 15.3 |
| Oxygen | 3.7 | 6.5 |
| Carbonic Oxide | 1.56 | 6.2 |
| Nitrogen | 1.56 | 4.1 |
| Hydrogen | 1.56 | 4.6 |

The estimate of Saussure is in general too high. That of Mr Dalton and Dr Henry for nitrous oxide is considerably beyond the truth, according to the experiments of Sir H. Davy.

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## *Deutoxide of Hydrogen.*

The deutoxide, or peroxide of hydrogen, was discovered by M. Thenard in the year 1818. Before describing the mode of preparing this compound, it must be observed that there are two oxides of barium, and that when the peroxide of that metal is put into water containing free muriatic acid, oxygen gas is set at liberty, and the peroxide is converted into the protoxide of barium or baryta, which combines with the acid. When this process is conducted with the necessary precautions, the oxygen which is set free, instead of escaping in the form of gas, unites with the hydrogen of the water, and brings it to a maximum of oxidation. For a full detail of all the minutiæ of the process, the reader may consult the original memoir of M. Thenard* ; the general directions are the following :—To six or seven ounces of water, add so much pure concentrated muriatic acid as is sufficient to dissolve 230 grains of baryta, and after having placed the mixed fluids in a glass vessel surrounded with ice, add in successive portions 185 grains of the deutoxide of barium reduced to powder, and stir with a glass rod after each addition. When the solution, which takes place without effervescence, is complete, sulphuric acid is added in sufficient quantity for precipitating the whole of the baryta in the form of an insoluble sulphate, so that the muriatic acid which had been combined with that earth is completely separated from it. Another portion of the deutoxide of barium, amounting to 185 grains, is then put into the liquid ; the free muriatic acid instantly acts upon it, and as soon as it is dissolved, the baryta is again converted into a sulphate by the addition of sulphuric acid. The solution is then filtered in order to separate the insoluble sulphate of baryta, and fresh quantities of the peroxide of barium are added in succession, till about three ounces have been employed. The liquid then contains from 25 to 30 times its volume of oxygen gas. The muriatic acid which has served to decompose the peroxide of barium during the whole process, is now removed by the cautious addition of the sulphate of silver, and the sulphuric acid afterwards separated by solid baryta.

The peroxide of hydrogen, as thus prepared, is still diluted with a considerable quantity of water. To separate the latter, the mixed liquids are placed under the exhausted receiver of an air pump, with a vessel of strong sulphuric acid. As the water evaporates, the density of the residue increases, till at last it acquires the specific gravity of 1.452. The concentration cannot be pushed further; for if kept under the receiver after reaching this point, the peroxide itself gradually but slowly volatilizes without change.

The peroxide of hydrogen of specific gravity 1.452 is a colourless transparent liquid without odour. It whitens the surface of the skin when applied to it, causes a prickling sensation, and even destroys its texture if the application is long continued. It acts in a similar manner on the tongue, in addition to which it thickens the saliva, and tastes like certain metallic solutions. Brought into contact with litmus and turmeric paper, it gradually destroys their colour and makes them white. It is slowly volatilized in vacuo, which shows that its vapour is much less elastic than that of water. It preserves its liquid form at all degrees of cold to which it has hitherto been exposed. At the temperature of 59° F. it is decomposed, being converted in-

* In the An. de Chim. et de Phys. vol. viii. ix. and x.; Annals of Philosophy vol. xiii. and xiv.; and M. Thenard's Traité de Chimie.

to water and oxygen gas. For this reason it ought to be preserved in glass tubes surrounded with ice.

The most remarkable property of the peroxide of hydrogen is the facility with which it is decomposed. The diffused daylight does not seem to exert any influence over it, and even the direct solar rays act upon it tardily. It effervesces from the escape of oxygen at 59° F. and the sudden application of a higher temperature, as of 212° F. gives rise to such rapid evolution of gas as to cause an explosion. Water, apparently by combining with the peroxide, renders it more permanent; but no degree of dilution can enable it to bear the heat of boiling water, at which temperature it is decomposed entirely. All the metals except iron, tin, antimony and tellurium, have a tendency to decompose the peroxide of hydrogen, converting it into oxygen and water. A state of minute mechanical division is essential for producing rapid decomposition. If the metal is in mass, and the peroxide diluted with water, the action is slow. The metals which have a strong affinity for oxygen are oxidized at the same time, such as potassium, sodium, arsenic, molybdenum, manganese, zinc, tungsten, and chromium; while others, such as gold, silver, platinum, iridium, osmium, rhodium, palladium, and mercury, retain the metallic state.

The peroxide of hydrogen is decomposed at common temperatures by many of the metallic oxides. That some of the protoxides should have this effect, would be anticipated in consequence of their tendency to pass into a higher state of oxidation. The protoxides of iron, manganese, tin, cobalt, and others, act on this principle, and are really converted into peroxides. The peroxides of barium, strontium and calcium may likewise be formed by the action of the peroxide of hydrogen on baryta, strontia and lime. But it is a singular fact, and I am not aware that any satisfactory explanation of it has been given, that some oxides decompose the peroxide of hydrogen without passing into a higher degree of oxidation. The peroxides of silver, lead, mercury, gold, platinum, manganese, and cobalt, possess this property in the greatest perfection, acting on the peroxide of hydrogen, when concentrated, with surprising energy. The decomposition is complete and instantaneous; oxygen gas is evolved so rapidly as to produce a kind of explosion, and such intense temperature is excited, that the glass tube in which the experiment is conducted becomes red-hot. The reaction is very great even when the peroxide of hydrogen is diluted with water. The oxide of silver occasions a very perceptible effervescence when put into water which contains only 1·50th of its bulk of oxygen. All the metallic oxides, which are decomposed by a red heat, such as those of gold, platinum, silver, and mercury, are reduced to the metallic state when they act upon the peroxide of hydrogen. This effect cannot be altogether ascribed to the caloric disengaged during the action; for the oxide of silver suffers reduction when put into a very dilute solution of the peroxide, although the decomposition is not then attended by an appreciable rise of temperature.

While the tendency of metals and metallic oxides is to decompose the peroxide of hydrogen, acids have the property of rendering it more stable. In proof of this, let a portion of that liquid, somewhat diluted with water, be heated till it begins to effervesce from the escape of oxygen gas; let some strong acid, as the nitric, sulphuric, or muriatic, be then dropped into it, and the effervescence will cease on the instant. When a little gold in a state of fine division is put into a weak solution of the peroxide of hydrogen, containing only 10, 20, or 30 times its bulk of oxygen, brisk effervescence ensues; but on letting one drop of sulphuric acid fall into it, the effervescence ceases instantly; it is reproduced by the addition of potassa, and is again arrested by adding a

second portion of acid. The only acids that do not possess this property are those that have a low degree of acidity, as the carbonic and boracic acids; or those which suffer a chemical change when mixed with the peroxide of hydrogen, such as the hydriodic and sulphurous acids, and sulphuretted hydrogen. Acids appear to increase the stability of the peroxide in the same way as water does, namely, by combining chemically with it. Several compounds of this kind were formed by Thenard, before he was aware of the existence of the peroxide of hydrogen. They were made by dissolving the peroxide of barium in some dilute acid, such as the nitric, and then precipitating the baryta by sulphuric acid. As the nitric acid was supposed under these circumstances to combine with an additional quantity of oxygen, Thenard applied the term oxygenized nitric acid to the resulting compound, and described several other new acids under a similar title. But the subsequent discovery of the peroxide of hydrogen put the nature of the oxygenized acids in a clearer light; for their properties are easily explicable on the supposition that they are composed, not of acids and oxygen gas, but of acids united with the peroxide of hydrogen.

The peroxide of hydrogen was analyzed by diluting a known weight of it with water, and then decomposing it by boiling the solution. According to two careful analyses, conducted on this principle, 864 parts of the peroxide of hydrogen are composed of 466 of water, and 398 of oxygen gas. The 466 of water contain 414 of oxygen, whence it may be inferred that the peroxide of hydrogen contains twice as much oxygen as water. A small deficiency of oxygen in the experiment was to be expected, owing to the difficulty of obtaining the peroxide of hydrogen perfectly free from water. The peroxide consists, therefore, of

| | | |
|---|---|---|
| Hydrogen | 1 | one proportion. |
| Oxygen | 16 | two proportions. |

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## SECTION V.

### *NITROGEN.*

The existence of nitrogen gas, as distinct from every other gaseous substance, appears to have been first noticed by the late Dr Rutherford in 1772. Lavoisier discovered in 1775 that it is a constituent part of the atmosphere, and the same discovery was made soon after, or about the same time, by Scheele. Lavoisier called it *Azote* from *α privative*, and ζωὴ life, because it is unable to support the respiration of animals; but as it possesses this negative property in common with most other gases, the more appropriate term *nitrogen* has been since applied to it, from the circumstance of its being an essential ingredient of nitric acid.

Nitrogen is most conveniently prepared by burning a piece of phosphorus in a jar full of air inverted over water. The strong affinity of phosphorus for oxygen enables it to burn till the whole of that gas is consumed. The product of the combustion, phosphoric acid, is at first diffused through the residue in the form of a white cloud; but as this substance is rapidly absorbed by water, it disappears entirely in the course of half an hour. The residual gas is nitrogen, containing a

small quantity of carbonic acid and vapour of phosphorus, both of which may be removed by agitating it briskly with a solution of pure potassa. Several other substances may be employed for withdrawing the oxygen from atmospheric air. A solution of the proto-sulphate of iron, charged with the deutoxide of nitrogen, absorbs the oxygen in the space of a few minutes. A stick of phosphorus produces the same effect in 24 hours, if exposed to a temperature of 60° F. A solution of the sulphuret of potassa or of lime acts in a similar manner; and a mixture of equal parts of iron filings and sulphur, made into a paste with water, may be employed with the same intention. Both these processes, however, are inconvenient from their slowness. Nitrogen gas may likewise be obtained by exposing a mixture of fresh muscle and nitric acid of specific gravity 1.20 to a moderate temperature. Effervescence then takes place, and a large quantity of gaseous matter is evolved, which is nitrogen mixed with a little carbonic acid. The latter must be removed by agitation with lime-water; but the residue still retains a peculiar odour, indicative of the presence of some volatile principle which cannot be wholly separated from it. The theory of this process is somewhat complex, and will be considered more conveniently in a subsequent part of the work.

Pure nitrogen is a colourless gas, wholly devoid of smell and taste. It does not change the blue colour of vegetables, and is distinguished from other gases more by negative characters than any striking quality. It is not a supporter of combustion; but, on the contrary, extinguishes all burning bodies that are immersed in it. No animal can live in it; but yet it exerts no injurious action either on the lungs or on the system at large, the privation of oxygen gas being the sole cause of death. It is not inflammable like hydrogen, though, under favourable circumstances, it may be made to unite with oxygen. Water, when deprived of air by ebullition, takes up about one and a half per cent of it. Its specific gravity is 0.9722*; and therefore 100 cubic inches at the mean temperature and pressure, will weigh 29.652 grains.

Considerable doubt exists as to the nature of nitrogen. Though ranked among the simple non-metallic bodies, some circumstances have led to the suspicion that it is compound, and this opinion has been warmly advocated by Sir H. Davy and Berzelius. The chief argument in favour of this view is drawn from the phenomena that attend the formation of what is called the *ammoniacal amalgam*. From the metallic appearance of this substance, it was supposed to be a compound of mercury and a metal; and as the only method of forming it is by the action of galvanism on a salt of ammonia, in contact with a globule of mercury, it follows that the metal, if present at all, must have been supplied by the ammonia. Now ammonia is composed of hydrogen and nitrogen; and as the former, from its levity, could hardly be supposed to contain a metal, it was inferred that it must be present in the latter. Unfortunately for this argument, the supposed metal cannot be obtained in a separate state. The amalgam no sooner ceases to be under the galvanic influence than its elements begin to separate spontaneously, and in a few minutes the decomposition is complete, the sole products being ammonia, hydrogen, and pure mercury. Sir H. Davy accounts for this change on the supposition that water is decomposed; that its oxygen reproduces nitrogen

* This number is calculated on the assumption that air consists of one measure of oxygen to four of nitrogen, and that 1.1111 is the specific gravity of oxygen gas. See Thomson's First Principles, vol. i. p. 99.

by uniting with the supposed metal; and that one part of its hydrogen forms ammonia by uniting with the nitrogen, while the remainder escapes in the form of gas. But Gay-Lussac and Thenard, (Recherches Physico-Chimiques, vol. i.) declare that the amalgam resolves itself into mercury, ammonia, and hydrogen, even though perfectly free from moisture; and infer from their experiments that it is composed of those three substances combined directly with one another. It hence appears that the examination of the ammoniacal amalgam affords no proof of the compound nature of nitrogen; nor was Sir H. Davy's attempt to decompose that gas by aid of potassium, intensely heated by a galvanic current, attended with better success. Berzelius has defended the idea that nitrogen is a compound body on other principles; but as his arguments, though very ingenious, are merely speculative, they cannot be admitted as decisive of the question.

## *On the Atmosphere.*

The earth is every where surrounded by a mass of gaseous matter called the atmosphere, which is preserved at its surface by the force of gravity, and revolves together with it around the sun. It is colourless and invisible; excites neither taste nor smell when pure, and is not sensible to the touch unless when it is in motion. It possesses the physical properties of elastic fluids in a high degree. The knowledge of its exact weight is an essential element in many physical and chemical researches, and has therefore been determined with much care. According to the experiments of Sir G. Shuckburgh Evelyn, 100 cubic inches of pure and dry atmospheric air at 60° F. and 30 Bar. weigh exactly 30.5 grains*. Its specific gravity is unity, being the standard with which the density of all other elastic fluids is compared. It is 828 times lighter than water, and near 11,260 times lighter than mercury.

The pressure of the atmosphere was first noticed early in the seventeenth century by Galileo, and was afterwards demonstrated by his pupil Torricelli, to whom science is indebted for the invention of the barometer. Its pressure at the level of the sea is equal to a weight of about 15 pounds on every square inch of surface, and is capable of supporting a column of water 34 feet high, and one of mercury of 30 inches; that is, a column of mercury one inch square and 30 inches long has the same weight (nearly 15 pounds) as a column of water of the same size and 34 feet long, and as a column of air of the same size reaching from the level of the sea to the extreme limit of the atmosphere. By the use of the barometer it was discovered that the atmospheric pressure is variable. It varies according to the elevation above the level of the sea, and on this principle the height of mountains is estimated. Supposing the density of the atmosphere to be uniform, a fall of one inch in the barometer would correspond to 11,260 inches or 938 feet of air; but in order to make the calculation with accuracy, allowance must be made for the increasing rarity of the air, and for various other circumstances which are detailed in works on meteorology. (Daniell's Meteorological Essays, 2d edit. 376.) From causes at present not understood, the pressure varies likewise at the same place. On this depends the indications of the barometer as a weather-glass; for observation has fully proved, that the weather is commonly fair and calm when the barometer is high, and usually wet and stormy when the mercury falls.

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* See note referring to Dr Prout's recent experiments on the weight of pure atmospheric air, page 99. B.

Atmospheric air is highly compressible and elastic; so that its particles admit of being approximated to a great extent by compression, and expand to an extreme degree of rarity, when the tendency of its particles to separate is not restrained by external force. It has been found experimentally that the volume of air and all other gaseous fluids, so long as they retain the elastic state, is inversely as the pressure to which they are exposed. Thus a portion of air which occupies 100 measures when compressed by a force of one pound, will be diminished to 50 measures when the pressure is doubled, and will expand to 200 measures when the compression is equal to half a pound. This law was first demonstrated in 1662 by the celebrated Boyle, and a second demonstration of it was given some years afterwards by the French philosopher M. Mariotte, apparently without being aware that the discovery had been previously made in England. It is hence frequently called the law of Mariotte. Till lately it had not been verified for very great pressures; but from the experiments of Oersted in 1825, who extended his observations to air compressed by a force equal to 110 atmospheres, it may be inferred to be quite general, except when the gaseous matter assumes the liquid form*. (Edinb. Journal of Science, No. VIII. p. 224.) At what pressure air undergoes this change is uncertain. Mr Perkins indeed states, that he has condensed it into a liquid by a pressure of 2000 atmospheres; but there appears good reason to suspect that the liquid obtained in this experiment was no other than water. It retained its liquid form under the atmospheric pressure, and therefore wanted the distinguishing character of a condensed gas.

The extreme compressibility and elasticity of the air accounts for the facility with which it is set in motion, and the velocity with which it is capable of moving. It is subject to the laws which characterize elastic fluids in general. It presses, therefore, equally on every side; and when some parts of it become lighter than the surrounding portions, the denser particles rush rapidly into their place and force the more rarefied ones to ascend. The motion of air gives rise to various familiar phenomena. A stream or current of air is wind, and an undulating vibration excites the sensation of sound.

The atmosphere is not of equal density at all its parts. This is obvious from the consideration, that those portions which are next the earth sustain the whole pressure of the atmosphere, while the higher strata bear only a part. The atmospheric column diminishes in length as the distance from the earth's surface increases; and, consequently, the greater the elevation, the lighter must be the air It is not known to what height the atmosphere extends. From calculations founded on the phenomena of refraction, its height is supposed to be about 45 miles; and Dr Wollaston estimates from the law of expansion of gases, that it must extend to at least 40 miles with properties unimpaired by rarefaction. In speculating on its extent beyond that distance, it becomes a question whether the atmosphere is or is not limited to the earth. This subject has been discussed with his usual sagacity by Dr Wollaston in an Essay on the Finite Extent of the Atmosphere, published in the Philosophical Transactions for 1822. On the supposition that the atmosphere is unlimited, it would pervade all space, and accumulate about the sun, moon, and planets, forming around each an atmosphere, the density of which would depend on their respective forces of attraction. Now Dr Wollaston infers from astronomical ob-

* See note, page 66. B.

servations made by himself and Captain Kater, that there is no solar atmosphere; and the observations of other astronomers appear to justify the same inference with respect to the planet Jupiter. If the accuracy of these conclusions be admitted, it follows that our atmosphere is confined to the earth; and it may next be asked, by what means is its extent limited? Dr Wollaston accounts for it, by supposing the air, after attaining a certain degree of rarefaction, to possess so feeble an elasticity, that the tendency of its particles to separate further from each other is counteracted by gravity. The unknown height at which this equilibrium between the two forces of elasticity and gravitation takes place, is the outermost boundary of the atmosphere. It is further argued, that this mode of reasoning is inapplicable unless the air be supposed to consist of ultimate atoms. Then only can each particle be separated from contiguous ones, to a degree sufficient for producing that diminution of elasticity required by the argument; for if the material substance of air is divisible without limit, each particle will in itself contain an infinite number of other particles, the tension of which, in consequence of their proximity, should lead to their mutual separation. The production of fresh portions of air would on this principle be endless.

In order to account for the limited nature of the atmosphere, according to this principle, the air is inferred to consist of atoms; and if the inference be granted, it is fair to presume that matter in general has a similar constitution. The tendency of Dr Wollaston's reasoning, therefore, is to demonstrate the truth of the atomic theory. But even admitting astronomical observations as conclusive against the existence of a solar atmosphere, and as proving by inference the extent of ours to be limited, it scarcely follows, I apprehend, that much weight can be attached to the argument. The tension or elasticity of gaseous matter is lessened by two causes, diminution of pressure, and reduction of temperature. The former alone is taken into account by Dr Wollaston; but as the tendency of the latter to deprive gases of their elastic form is now fully established, it appears to me that the extreme cold which is admitted to prevail in the higher regions of the air, may of itself be a condition sufficient to put a limit to the extent of the atmosphere. Some very ingenious remarks have been made on this subject by Mr Graham. (Philos. Mag. and Annals, i. 107.)

The temperature of the atmosphere varies with its elevation. Gaseous fluids permit radiant matter to pass freely through them without any absorption, and therefore without their temperature being influenced by its passage. The atmosphere is not heated by transmitting the rays of the sun. The air receives its caloric solely from the earth, and chiefly by actual contact; so that its temperature becomes progressively lower, as the distance from the general mass of the earth increases. Another circumstance which contributes towards the same effect, is the increasing tenuity of the atmosphere; for the temperature of rarefied air is less raised by a given quantity of heat, than that of the same portion of air when compressed, owing to its specific caloric being greater in the former state than in the latter. From the joint influence of both these causes it is found that, in ascending into the atmosphere, the temperature diminishes at the rate of one degree for about every 300 feet. The rate of decrease is probably much slower at considerable distances from the earth; but still there is no reason to doubt that the temperature continues to decrease with the increasing elevation. There must consequently in every latitude be a point, where the thermometer never rises above 32°, and where ice is never liquefied. This point varies with the latitude, being highest within

the topics, and descending gradually as we advance towards the poles. The following table, from the supplement to the Encyclopedia Britannica, page 190, article climate, shows the point of perpetual ice corresponding to different latitudes.

| *Latitude.* | *English feet in height.* | *Latitude.* | *English feet in height.* |
|---|---|---|---|
| 0° | 15,207 | 45° | 7,671 |
| 5° | 15,095 | 50° | 6,334 |
| 10° | 14,764 | 55° | 5,034 |
| 15° | 14,220 | 60° | 3,818 |
| 20° | 13,478 | 65° | 2,722 |
| 25° | 12.557 | 70° | 1,778 |
| 30° | 11,484 | 75° | 1,016 |
| 35° | 10,287 | 80° | 457 |
| 40° | 9,001 | 85° | 117 |

Air was one of the four elements of the ancient philosophers, and their opinion of its nature prevailed generally till its accuracy was rendered questionable by the experiments of Boyle, Hooke, and Mayow. The discovery of oxygen gas in 1774 paved the way to the knowledge of its real composition, which was discovered about the same time by Scheele and Lavoisier. The former exposed some atmospheric air to a solution of the sulphuret of potassa, which gradually absorbed the whole of the oxygen. Lavoisier effected the same object by the combustion of iron wire and phosphorus.

The earlier analyses of the air did not agree very well with one another. According to the researches of Lavoisier, it is composed of twenty-seven measures of oxygen to seventy-three of nitrogen. The analysis of Scheele gave a somewhat higher proportion of oxygen. Priestley found that the quantity of oxygen varies from twenty to twenty-five per cent; and Cavendish estimated it only at twenty. These discrepancies must have arisen from imperfections in the mode of analysis; for the proportion of oxygen has been found by subsequent experiments to be almost, if not exactly, that which was stated by Mr Cavendish. The results of Scheele and Priestley are clearly referrible to this cause. It is now known that the processes they employed cannot be relied on, unless certain precautions are taken of which those chemist were ignorant. Recently boiled water absorbs nitrogen; and, consequently, if the sulphuret of potassa be dissolved in that liquid by the aid of heat, the solution takes up a portion of nitrogen during the process, and thereby renders the apparent absorption of oxygen too great. This inconvenience may be avoided by dissolving the alkaline sulphuret in cold unboiled water. The deutoxide of nitrogen, employed by Priestley, removes all the oxygen in the course of a few seconds; but for reasons which will soon be mentioned, its indications are very apt to be fallacious. The combustion of phosphorus, as well as the gradual oxidation of that substance, acts in a very uniform manner, and removes the whole of the oxygen completely. The residual nitrogen contains a little of the vapour of phosphorus, which increases the bulk of that gas by 1-40th, for which an allowance must be made in estimating the real quantity of nitrogen.

Since chemists have learned the precautions to be taken in the analysis of the air, a close correspondence has been observed in the results of their experiments upon it. The researches of Davy, Dalton, Gay-Lussac, Thomson, and others, leave no doubt that 100 measures, of pure atmospheric air consist of twenty or twenty-one volumes of oxygen, and eighty or seventy-nine of nitrogen. Dr Thomson, whose

analysis is the most recent, fixes the quantity of oxygen at twenty per cent; and the reasons he has assigned for regarding this estimate as more accurate than the other, appear satisfactory. The oxygen was determined (First Principles of Chemistry, vol. i. p. 97,) by mixing with the air a quantity of hydrogen, sufficient to convert all the oxygen present into water, and kindling the mixture by the electric spark. Water is formed and is condensed; and since that liquid is composed of one volume of oxygen to two of hydrogen, one-third of the diminution must give the exact quantity of oxygen. This process is so easy of execution, and so uniform in its indications, that it is now employed nearly to the total exclusion of all others*.

Such is the constitution of pure atmospheric air. But the atmosphere is never absolutely pure; for it always contains a certain variable quantity of carbonic acid and watery vapour, besides the odoriferous matter of flowers and other volatile substances, which are also frequently present. The carbonic acid never exceeds one in 100 parts, provided there is a free circulation of air, and generally amounts only to 1-1000th or 1-2000th of the whole. Saussure found it in air collected at the top of Mont-Blanc; and, indeed, it exists at all altitudes which have been hitherto attained.

The chief chemical properties of the atmosphere are owing to the presence of oxygen gas. Air from which this principle has been withdrawn is nearly inert. It can no longer support respiration and combustion, and metals are not oxidized by being heated in it. Most of the spontaneous changes which mineral and dead organized matters undergo, are owing to the powerful affinities of oxygen. The uses of nitrogen are in a great measure unknown. It was supposed to act as a mere diluent to the oxygen; but it most probably serves some useful purpose in the economy of animals, the exact nature of which has not been discovered.

The knowledge of the composition of the air, and of the importance of oxygen to the life of animals, naturally gave rise to the notion that the healthiness of the air, at different times, and in different places, depends on the relative quantity of this gas. It was, therefore, supposed that the purity of the atmosphere, or its fitness for communicating health and vigour, might be discovered by determining the propor-

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* The best analyses of atmospheric air correspond so nearly with the proportions of two volumes of nitrogen to half a volume of oxygen, that it seems probable that these proportions (which correspond at the same time with the theory of volumes) would be obtained exactly, if our experiments could be performed with rigid accuracy. On the assumption that these are the true proportions, the specific gravity of oxygen would be 1.1111, and that of nitrogen 0.9722. The reader may judge how far these calculated numbers may be depended on, by observing how nearly they coincide with the experimental numbers of Berzelius, the most accurate chemist of the present day. This philosopher, in conjunction with M. Dulong, determined the specific gravity of oxygen to be 1.1026, and that of nitrogen 0.976. The composition of atmospheric air, when stated in volumes, gives the oxygen at 20 per cent, as mentioned by Dr Turner; and yet the usual analyses make it 21 per cent. This discrepancy will probably disappear when the analysis is performed with more accuracy. Dr Hare found that the average of a great number of analyses of atmospheric air performed by explosion with hydrogen, by means of his very accurate eudiometers, gave the proportion of oxygen at 20.66 per cent, which approaches very nearly to the quantity indicated by the theory of volumes. B.

tion of oxygen; and hence the origin of the term *Eudiometer*, which was applied to the apparatus for analyzing the air. But this opinion, though at first supported by the discordant results of the earlier analysts, was soon proved to be fallacious. It appears, on the contrary, that the composition of the air is not only constant in the same place, but is the same in all regions of the earth, and at all altitudes. Air collected at the summit of the highest mountains, such as Mont-Blanc and Chimborazo, contains the same proportion of oxygen as that of the lowest valleys. The air of Egypt was found by Berthollet to be similar to that of France. The air which Gay-Lussac brought from an altitude of 21,735 feet above the earth, had the same composition as that collected at a short distance from its surface. Even the miasmata of marshes, and the effluvia of infected places, owe their noxious qualities to some principle of too subtile a nature to be detected by chemical means, and not to a deficiency of oxygen. Seguin examined the infectious atmosphere of an hospital, the odour of which was almost intolerable, and could discover no appreciable deficiency of oxygen, or other peculiarity of composition.

The question has been much discussed whether the oxygen and nitrogen gases of the atmosphere are simply mixed, or chemically combined with one another. Appearances are at first view greatly in favour of the latter opinion. Oxygen and nitrogen gases differ in density, and therefore it might be expected, were they merely mixed together, that the oxygen, as the heavier gas, ought, in obedience to the force of gravity, to collect in the lower regions of the air, while the nitrogen should have a tendency to occupy the higher. But this has nowhere been observed. If air be confined in a long tube, preserved at perfect rest, its upper part will contain just as much oxygen as the lower, even after an interval of many months; nay, if the lower part of it be filled with oxygen, and the upper with nitrogen, these gases will be found in the course of a few hours to have mixed intimately with one another. The constituents of the air are, also, in the exact proportion for combining. By measure they are in the simple ratio of one to four, which agrees perfectly with the law of combination by volume; and by weight they are as 8 to 28, which is one proportion of oxygen to two of nitrogen.

Strong as are these arguments in favour of the chemical theory, it is nevertheless liable to objections which appear insuperable. The atmosphere possesses all the characters that should arise from a mechanical mixture. There is not, as in all other cases of chemical union, any change in the bulk, form, or other qualities of its elements. The nitrogen manifests no attraction for the oxygen. All bodies which have an affinity for oxygen, abstract it from the atmosphere with as much facility as if the nitrogen was absent altogether. Even water effects this separation; for the air which is expelled from rain water by ebullition, contains more than twenty per cent. of oxygen. When oxygen and nitrogen gases are mixed together in the ratio of one to four, the mixture occupies precisely five volumes, and has every property of pure atmospheric air. The refractive power of the atmosphere is precisely such as a mixture of oxygen and nitrogen gases ought to have; and different from what would be expected were its elements chemically united. (Edinburgh Journal of Science, No. 8, page 211.)

Since the elements of the air cannot be regarded as in a state of actual combination, it is necessary to account for the steadiness of their proportion on some other principle. Chemists are divided on this subject between two opinions. It is conceived, according to one

view, that the affinity of oxygen and nitrogen for one another, though insufficient to cause their combination when mixed together at ordinary temperatures, may still operate in such a manner as to prevent their separation; that a certain degree of attraction is even then exerted between them, which is able to counteract the tendency of gravity. An opinion of this kind was advanced by Berthollet, in his *Statique Chimique*, and defended by the late Dr Murray. This doctrine, however, is not satisfactory. It is, indeed, quite conceivable that oxygen and nitrogen may attract each other in the way supposed; and it may be admitted that this supposition explains why these two gases continue in a state of perfect mixture. But still the explanation is unsatisfactory, and for the following reason:—Mr Dalton took two cylindrical vessels, one of which was filled with carbonic acid, the other with hydrogen gas; the latter was placed perpendicularly over the other, and a communication was established between them. In the course of a few hours hydrogen was detected in the lower vessel, and carbonic acid in the upper. If the upper vessel be filled with oxygen, nitrogen, or any other gas, the same phenomena will ensue; the gases will be found, after a short interval, to be in a state of mixture, and will at last be distributed equally through both vessels. Now this result cannot, with any shadow of reason, be ascribed to the action of affinity. It is well known that carbonic acid cannot be made to unite either with hydrogen, oxygen, or nitrogen; and, therefore, it is quite gratuitous to assert that it has an affinity for them. Some other power must be in operation, capable of producing the mixture of gases with one another, independently of chemical attraction; and if this power can cause carbonic acid to ascend through a gas which is twenty-two times lighter than itself, it will surely explain why oxygen and nitrogen gases, the densities of which differ so little, should mix together in the atmosphere.

The explanation which Mr Dalton has given* of these phenomena, is founded on the assumption that the particles of one gas, though highly repulsive to each other, do not repel those of a different kind. It follows from this supposition, that one gas acts as a vacuum with respect to another; and, therefore, if a vessel full of carbonic acid be made to communicate with another of hydrogen, the particles of each gas insinuate themselves between the particles of the other, till they are equally diffused through both vessels. The particles of the carbonic acid do not indeed fill the space occupied by the hydrogen with the same velocity as if it were a real vacuum; because the particles of the hydrogen afford a mechanical impediment to their progress. The ultimate effect, however, is the same as if the vesssel of hydrogen had been a vacuum.

Though it would not be difficult to find objections to this hypothesis, it has the merit of being applicable to every possible case; which cannot, I conceive, be admitted of the other. It accounts not only for the mixture of gases, but for the equable diffusion of vapours through gases, and through each other.

There is still one circumstance for consideration respecting the atmosphere. Since oxygen is necessary to combustion, to the respiration of animals, and to various other natural operations, by all of which that gas is withdrawn from the air, it is obvious that its quantity would gradually diminish, unless the tendency of those causes was counteracted by some compensating process. To all appearance there does

* Manchester Memoirs, vol. v.

exist some source of compensation; for chemists have not hitherto noticed any change in the constitution of the atmosphere. The only source by which oxygen is known to be supplied, is by the action of growing vegetables. A healthy plant absorbs carbonic acid during the day, appropriates the carbonaceous part of that gas to its own wants, and evolves the oxygen with which it was combined. During the night, indeed, an opposite effect is produced. Oxygen gas then disappears, and carbonic acid is eliminated; but it follows from the experiments of Priestley and Davy, that plants during 24 hours yield more oxygen than they consume. Whether living vegetables make a full compensation for the oxygen removed from the air by the processes above mentioned, is uncertain. From the great extent of the atmosphere, and the continual agitation to which its different parts are subject by the action of winds, the effects of any deteriorating process would be very gradual, and a change in the proportion of its elements could be perceived only by observations made at very distant intervals.

## *Compounds of Nitrogen and Oxygen.*

Chemists are acquainted with five compounds of nitrogen and oxygen, the composition of which, as deduced from the researches of Gay-Lussac, Dr Henry, and Sir H. Davy, is as follows:

| | *By Volume.* | | *By Weight.* | |
|---|---|---|---|---|
| | *Nitrogen.* | *Oxygen.* | *Nitrogen.* | *Oxygen.* |
| Nitrous oxide | 100 | 50 | 14 | 8 |
| Nitric oxide | 100 | 100 | 14 | 16 |
| Hyponitrous acid | 100 | 150 | 14 | 24 |
| Nitrous acid | 100 | 200 | 14 | 32 |
| Nitric acid | 100 | 250 | 14 | 40 |

The first of these, as containing the smallest quantity of oxygen, is regarded as a compound of one proportion, or according to the atomic theory of one atom, of each element. The atomic weight of nitrogen, that of oxygen being 8, will, therefore, be 14. The other four compounds must consequently be composed of one atom of nitrogen, united in the second with two, in the third with three, in the fourth with four, and in the fifth with five, atoms of oxygen.

## *Protoxide of Nitrogen.*

This gas was discovered by Priestley, who gave it the name of *dephlogisticated nitrous air*. Sir H. Davy called it *nitrous oxide*. According to the principles of chemical nomenclature, its proper appellation is *protoxide of nitrogen*. It may be formed by exposing nitric oxide for some days to the action of iron filings, or other substances which have a strong affinity for oxygen. The nitric oxide loses one half of its oxygen, and is converted into the protoxide. But the most convenient method of procuring it, is by means of the nitrate of ammonia. When this salt is exposed to a temperature of 400° or 500° F. it liquefies, bubbles of gas begin to rise from it, and in a short time brisk effervescence ensues, which continues till the whole of the salt disappears The nitrate of ammonia should be contained in a glass retort, and the heat applied by means of a lamp placed at such a distance below it as to maintain a moderately rapid evolution of gas.

The sole products of this operation, when carefully conducted, are

water and the protoxide of nitrogen. The theory of the process is as follows:—

Nitrate of ammonia is composed of

| | | |
|---|---|---|
| Nitric acid | 54 | one proportion. |
| Ammonia | 17 | one proportion. |
| | 71 | |

Nitric acid consists of

| | | |
|---|---|---|
| Nitrogen | 14 | one proportion. |
| Oxygen | 40 | five proportions. |
| | 54 | |

And ammonia of

| | | |
|---|---|---|
| Nitrogen | 14 | one proportion. |
| Hydrogen | 3 | three proportions. |
| | 17 | |

By the action of heat these elements arrange themselves in a new order. The hydrogen takes so much oxygen as is sufficient for forming water, and the residual oxygen converts the nitrogen both of the nitric acid and of the ammonia into the protoxide of nitrogen. The decomposition of 71 grains of the salt will therefore yield

| | | | |
|---|---|---|---|
| Water . . | 27, or three pr. | Oxygen | 24, or three pr. |
| | | Hydrogen | 3, or three pr. |
| Protoxide of Nitrogen | 44, or two pr. | Oxygen | 16, or two pr. |
| | | Nitrogen | 28, or two pr. |
| | 71 | | |

The protoxide of nitrogen is a colourless gas, which does not affect the blue vegetable colours, even when mixed with atmospheric air. Recently boiled water, which has cooled without exposure to the air, absorbs nearly its own bulk of it at 60° F, and gives it out again unchanged by boiling. The solution, like the gas itself, has a faint odour and sweet taste. The action of water upon it affords a ready means of testing its purity, removing it readily from all other gases, such as oxygen and nitrogen, which are sparingly absorbed by that liquid. For the same reason it cannot be preserved over cold water; but should be collected either over hot water or mercury.

The protoxide of nitrogen is a supporter of combustion. Most substances burn in it with far greater energy than in the atmosphere. When a recently extinguished candle with a very red wick is introduced into it, the flame is instantly restored. Phosphorus, if previously kindled, burns in it with great brilliancy. Sulphur, when burning feebly, is extinguished by it; but if it is immersed while the combustion is lively, the size of the flame is increased considerably. With an equal bulk of hydrogen it forms a mixture which explodes violently by the electric spark or by flame. In all these cases the product of combustion is the same as when oxygen gas or atmospheric air is used. The protoxide is decomposed; the combustible matter unites with its oxygen, and the nitrogen is set free. The protoxide of nitrogen suffers decomposition when a succession of electric sparks is passed through it. A similar effect is caused by conducting it through a porcelain tube heated to incandescence. It is resolved in both instances, into nitrogen, oxygen, and nitrous acid.

Sir H. Davy discovered* that the protoxide of nitrogen may be

* Researches on the Nitrous Oxide.

taken into the lungs with safety, and that it supports respiration for a few minutes. He breathed nine quarts of it, contained in a silk bag, for three minutes, and twelve quarts for rather more than four; but no quantity could enable him to bear the privation of atmospheric air for a longer period. Its action on the system, when inspired, is very remarkable. A few deep inspirations are followed by most agreeable feelings of excitement, similar to the early stages of intoxication. This is shown by a strong propensity to laughter, by a rapid flow of vivid ideas, and an unusual disposition to muscular exertion. These feelings, however, soon subside, and the person returns to his usual state without experiencing the languor or depression which so universally follows intoxication from spirituous liquors. Its effects, however, on different persons, are various; and in individuals of a plethoric habit, it sometimes produces giddiness, headach, and other disagreeable symptoms.

The protoxide of nitrogen was analyzed by Sir H. Davy by means of hydrogen gas. He mixed 39 measures of the former with 40 measures of hydrogen, and fired the mixture by the electric spark. Water was formed, and the residual gas, which amounted to 41 measures, had the properties of pure nitrogen. As 40 measures of hydrogen require 20 of oxygen for combustion, it follows that 39 volumes of the protoxide of nitrogen contain 41 of nitrogen and 20 of oxygen. But since no exception has hitherto been found to Gay-Lussac's law of gaseous combination, it may be inferred that the protoxide of nitrogen contains its own bulk of nitrogen and half its volume of oxygen. The recent analysis of this compound by Dr Henry, (Annals of Phil. viii. 299, N.S.) performed by means of carbonic oxide gas, has proved beyond a doubt that this is the exact proportion. Now,

| | | | | |
|---|---|---|---|---|
| 100 | cubic inches of | nitrogen weigh | 29.652 | grains. |
| 50 | do | oxygen | 16.944 | |
| These numbers added together amount to | | | 46.596 | |

which must be the weight of 100 cubic inches of the protoxide; and its specific gravity is, therefore, 1.5277. Its composition by weight is determined by the same data, being 16.944 of oxygen to 29.652 of nitrogen, or as 8 to 14. Its atomic weight is, of course, 8+14, or 22.

## *Deutoxide of Nitrogen.*

The deutoxide of nitrogen is best obtained by the action of nitric acid, of specific gravity 1.2, on metallic copper.. Brisk effervescence takes place, without the aid of heat, and the gas may be collected over water or mercury. The copper gradually disappears during the process; the liquid acquires a beautiful blue colour, and yields on evaporation a salt which is composed of nitric acid and peroxide of copper. The chemical changes that occur are the following.—One portion of nitric acid suffers decomposition. Part of its oxygen unites with the copper, and converts it into the peroxide; while another part is retained by the nitrogen of the nitic acid, forming the deutoxide of nitrogen. The peroxide of copper attaches itself to some undecomposed nitric acid, and forms the blue nitrate of copper. Many other metals are oxidized by nitric acid, with the disengagement of a similar compound; but none, mercury excepted, yields so pure a gas as copper.

The gas derived from this source was discovered by Dr Hales. It was first carefully studied by Priestley, who called it *nitrous air*.

The terms *nitrous gas*, and *nitric oxide*, are frequently applied to it; but the *deutoxide of nitrogen*, as indicative of its nature, is the most suitable appellation.

The deutoxide of nitrogen is a colourless gas. When mixed with atmospheric air, or any gaseous mixture that contains oxygen in an uncombined state, dense, suffocating, acid vapours, of a red or orange colour are produced, called nitrous acid vapours; which are copiously absorbed by water, and communicate acidity to it. The deutoxide may be distinguished by this character from every other substance, and for the same reason affords a convenient test of the presence of free oxygen. Though it gives rise to an acid by combining with oxygen, the deutoxide of nitrogen itself does not redden the blue colour of vegetables; but for this experiment, the gas must be well washed with water to separate all traces of nitrous acid. Water absorbs the deutoxide sparingly;—100 measures of that liquid, cold and recently boiled, take up about 11 of the gas.

Very few inflammable substances burn in the deutoxide of nitrogen. Burning sulphur, and a lighted candle are instantly extinguished by it. Charcoal and phosphorus, however, if in a state of vivid combustion at the moment of being immersed in it, burn with increased brilliancy. The product of the combustion is carbonic acid in the first case, and phosphoric acid in the second, nitrogen being separated in both instances. With an equal bulk of hydrogen, it forms a mixture which cannot be made to explode, but which is kindled by contact with a lighted candle, and burns rapidly with a greenish-white flame. Water and pure nitrogen are the products.

The deutoxide of nitrogen is quite irrespirable, exciting a strong spasm of the glottis, as soon as an attempt is made to inhale it. The experiment, however, is a dangerous one; for if the gas did reach the lungs, it would there mix with atmospheric air, and be converted into nitrous acid vapours, which are highly irritating and corrosive.

The deutoxide of nitrogen is partially resolved into its elements by being passed through red-hot tubes. A succession of electric sparks has a similar effect. It is converted into the protoxide of nitrogen by substances which have a strong affinity for oxygen, such as iron filings, and the alkaline sulphurets. Its composition was ascertained by Sir H. Davy by the combustion of charcoal. Two volumes of the deutoxide yielded one volume of nitrogen, and about one of carbonic acid*; whence it was inferred to consist of equal measures of oxygen and nitrogen gases united without any condensation. Gay-Lussac proved in his essay in the *Memoires d' Arcueil*, that this proportion is rigidly exact. He decomposed 100 measures of the gas, by heating potassium in it; 50 measures of pure nitrogen were left, and the loss of weight corresponded to 50 measures of oxygen. The same fact has been lately proved by Dr Henry in the paper already referred to. From these data, its composition by weight, and its specific gravity, may be determined by a simple calculation:—

| | | |
|---|---|---|
| 50 | cubic inches of oxygen weigh | 16.944 grains. |
| 50 | . . nitrogen | 14.826 |
| | | 31.770 |

Hence 100 cubic inches of the deutoxide of nitrogen, at the mean temperature and pressure, weigh 31.77 grains; and its specific gravity is, therefore, 1.0416. This is nearly the mean density of the deutoxide, as determined directly by Davy, Thomson, and Bérard, which

* Elements of Chemical Philosophy, p. 200.

confirms the accuracy of the data on which the calculation is founded. The elements of the deutoxide are obviously in the ratio, by weight, of 14 of nitrogen to 16 of oxygen; that is, one proportion of the first to two of the second. An equivalent of the compound is, therefore, $14+16=30$.

From the invariable formation of the red coloured acid vapours, whenever the deutoxide of nitrogen and oxygen are mixed together, these gases detect the presence of each other with great certainty; and since the product is wholly absorbed by water, one may be entirely removed from any gaseous mixture, by adding a sufficient quantity of the other. Priestley, who first observed this fact, supposed that combination takes place between them in one proportion only; and inferring on this supposition, that a given absorption would always indicate the same quantity of oxygen, he was led to employ the deutoxide of nitrogen in eudiometry. But in this opinion he was mistaken. The discordant results that were obtained by his method soon excited suspicion of its accuracy; and the source of error has since been discovered by the researches of Dalton and Gay-Lussac. It appears from the experiments of Gay-Lussac, and his results do not differ materially from those of Mr Dalton, that for 100 measures of oxygen, 400 of the deutoxide may be absorbed as a maximum, and 133 as a minimum; and that between these extremes, the quantity of the deutoxide corresponding to 100 of oxygen, is exceedingly variable. It does not follow from this, that oxygen and the deutoxide of nitrogen can unite in every proportion within these limits. The true explanation is, that the mixture of these gases may give rise to three compounds, the hyponitrous, nitrous, and nitric acids; and that either may be formed almost, if not entirely, to the exclusion of the others, if certain precautions are adopted. But in the usual mode of operating, two if not all are generated at the same time, and in a proportion to one another which is by no means uniform. The circumstances that influence the degree of absorption, when a mixture of oxygen and the deutoxide of nitrogen is made over water, are the following: —1, The diameter of the tube; 2, The rapidity with which the mixture is made; 3, The relative proportion of the two gases; 4, The time allowed to elapse after mixing them; 5, Agitation of the tube; and lastly, The opposite conditions of adding the oxygen to the deutoxide, or the deutoxide to the oxygen.

Notwithstanding these many sources of error, Dalton and Gay-Lussac maintain that the deutoxide of nitrogen may nevertheless be employed in eudiometry; and they have described the precautions which are required to ensure accuracy. Mr Dalton has given his process in the 10th volume of the Annals of Philosophy, page 38; and further directions have been published by Dr Henry in his Elements. The method of Gay-Lussac, to which my own observation would lead me to give the preference, may be found in the 2d volume, page 247, of the *Memoires d'Arcueil.* Instead of employing a narrow tube, such as is commonly used for measuring gases, Gay-Lussac advises that 100 measures of air should be introduced into a very wide tube or jar, and that an equal volume of the deutoxide of nitrogen should then be added. The red vapours, which are instantly produced, disappear very quickly, and the absorption after half a minute, or a minute at the most, may be regarded as complete. The residue is then passed into a graduated tube and measured. The diminution almost always, according to Gay-Lussac, amounts to 84 measures, one-fourth of which is oxygen*.

* On the supposition, in this experiment, that the oxygen and deut-

Gay-Lussac has applied this process to the analysis of various mixed gases, in which the oxygen was sometimes in a greater, at others in a less proportion than in the atmosphere, and the indications were always correct. When the proportion of oxygen is great, a proportionably large quantity of the deutoxide must of course be employed, in order that an excess of it might be present.

There is another mode of absorbing oxygen by means of the deutoxide of nitrogen. If a current of the deutoxide be conducted into a solution of the protosulphate of iron, the gas is absorbed in large quantity, and the solution acquires a deep olive-brown colour, which appears almost black when fully saturated. This solution absorbs oxygen with facility. But it cannot be safely employed in eudiometry; because the absorption of oxygen is accompanied, or at least very soon followed, by an evolution of gas from the liquid itself.

Sir H. Davy ascertained that the deutoxide of nitrogen is dissolved directly by the solution of iron, in the cold, without decomposition; and that when the solution is heated, the greater part of the gas is disengaged, and the remainder decomposed. The decomposition is determined chiefly by the affinity of the protoxide of iron for oxygen gas. The protoxide of iron decomposes a portion of water and of the deutoxide of nitrogen at the same time, and unites with the oxygen of both; while the hydrogen of the water, and the nitrogen of the deutoxide combine together, and generate ammonia. Nitric acid is formed when the solution is exposed to the air or oxygen gas, but not otherwise.

## *Hyponitrous Acid.*

On adding an excess of deutoxide of nitrogen to oxygen gas, confined in a glass tube over mercury, Gay-Lussac observed that the absorption is always uniform, provided a strong solution of pure potassa is put into the tube before mixing the two gases. He found that 100

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oxide of nitrogen unite in the proportions to form nitrous acid, one-third, and not one-fourth, of the diminution ought to be due to oxygen; for nitrous acid is composed of one volume of oxygen and two volumes of deutoxide of nitrogen. It may be asked, therefore, what are the real products of the experiment; as, in point of fact, one-fourth of the gaseous matter which disappears is due to oxygen? The late Dr Dana ingeniously reconciled this result with the theory of volumes, by supposing that two-thirds of the deutoxide of nitrogen become hyponitrous acid, and one-third, nitrous acid. Thus supposing six volumes of the deutoxide to be mixed with a sufficient quantity of oxygen, four volumes are assumed to be converted into hyponitrous acid, by combining with one volume of oxygen, and the remaining two, into nitrous acid by uniting with the same quantity of oxygen. In this manner six volumes of deutoxide and two volumes of oxygen, in all eight volumes, will disappear, being condensed, as above explained, into hyponitrous acid and nitrous acid. Now of these eight volumes, it is apparent that two volumes, or one-fourth, are oxygen.

When this experiment is performed with certain precautions, nitrous acid is the sole product, and the formula for calculating the quantity of oxygen, is of course to divide the deficit by three. I had the pleasure of seeing this proved experimentally, on several occasions, by Dr Hare of the University of Pennsylvania. B.

measures of oxygen gas combine under these circumstances with 400 of the deutoxide, forming an acid which unites with the potassa. The compound so formed is the hyponitrous acid, the composition of which may be easily inferred from the proportions just mentioned. For as the deutoxide of nitrogen contains half its volume of oxygen gas, the new acid must be composed of 200 measures of nitrogen to 300 of oxygen, or of 100 to 150. It contains, therefore, three times as much oxygen as the protoxide of nitrogen; so that, by weight, it is formed of

| | | |
|---|---|---|
| Nitrogen | 14 | one proportion. |
| Oxygen | 24 | three proportions. |

and its proportional number is 38.

Another method of forming the hyponitrous acid is by keeping the deutoxide of nitrogen for three months in a glass tube over mercury, in contact with a concentrated solution of pure potassa. The deutoxide is resolved into hyponitrous acid, which unites with the potassa, and into the protoxide of nitrogen which remains in the tube.

The hyponitrous acid has not hitherto been obtained in a free state. When an acid is added to the hyponitrite of potassa, the hyponitrous acid, instead of being dissolved by the water of the solution, suffers decomposition, and is converted, according to Gay-Lussac, into nitrous acid, and the deutoxide of nitrogen.

## *Nitrous Acid.*

To form pure nitrous acid by the mixture of oxygen gas with the deutoxide of nitrogen, the operation must not be conducted over water or mercury. The presence of the former determines the production of nitric acid; the latter is oxidized by the nitrous acid, and therefore decomposes it. Sir H. Davy made this compound by mixing two measures of the deutoxide of nitrogen and one of oxygen, free from moisture, in a dry glass vessel, previously exhausted by the air-pump. (Elements, p. 261.) Nitrous acid vapours were produced, and a contraction ensued, amounting to about one-half the volume of the mixed gases. The experiments of Gay-Lussac (An. de Ch. et de Ph. vol. i.) were similar in principle. He agrees with Sir H. Davy as to the proportion of the two gases, but is of opinion that they condense, in uniting, to 1-3d of their original volume. The conclusions of those chemists respecting the composition of nitrous acid have been confirmed by the researches of Dulong. [An. de Ch. et de Ph. vol. ii.) It is composed therefore of

| | *By Volume.* | *By Weight.* | |
|---|---|---|---|
| Nitrogen | 100 | 14 | or one equivalent. |
| Oxygen | 200 | 32 | or four equivalents. |

and its combining proportion is $32+14=46$.

The nitrous acid vapour is characterized by its orange-red colour. It is quite irrespirable, exciting great irritation and spasm of the glottis, even when moderately diluted with air. A taper burns in it with considerable brilliancy. It extinguishes burning sulphur; but the combustion of phosphorus continues in it with great vividness.

Nitrous acid may exist in the liquid as well as in the gaseous form. The liquid acid is most conveniently prepared by exposing the crystalized nitrate of lead, carefully dried, to a low red heat. The nitric acid of the salt is by this means resolved into nitrous acid and oxygen, and if the products are received in vessels kept moderately cool, the greater part of the former is condensed into a liquid. This substance

was first obtained by Gay-Lussac, who regarded it as hyponitrous acid, and described it as such in the essay above referred to; but M. Dulong has proved, by a careful analysis, that it is in reality anhydrous nitrous acid. Dulong procured it by mixing the deutoxide of nitrogen and oxygen gases in the ratio of 2 to 1, and exposing the nitrous acid vapours to a low temperature.

The liquid anhydrous acid has the following properties.—It is powerfully corrosive, has a strong acid taste and pungent odour, and is of a yellowish-orange colour. Its density is 1.451. It preserves the liquid form at the ordinary temperature and pressure, and boils at 82° F. Exposed to the atmosphere, it evaporates with great rapidity, forming the common nitrous acid vapours, which, when once mixed with air or other gases, require intense cold for condensation.

The action of water on the anhydrous nitrous acid is very remarkable. On mixing it with a large quantity of water, it is instantly resolved into nitric acid and the deutoxide of nitrogen; the former unites with the water, making a colourless solution, while the greater part of the latter escapes in the form of gas. When nitrous acid is added to a very small quantity of water, none of the deutoxide is disengaged; and a green coloured liquid is produced. If instead of employing a very large or a very small proportion of water, the anhydrous acid be dropped into a moderate quantity of that fluid, the disengagement of the deutoxide of nitrogen, at first considerable, becomes less and less at each addition of the acid, till at last the evolution of gas ceases altogether. The colour of the solution varies considerably during the experiment. From being quite colourless, the liquid acquires a greenish-blue tinge, thence passes into green of various depths of shade, and at length becomes of a yellowish-orange,—the colour of nitrous acid itself.

These changes are of a complicated nature, and may be accounted for in different ways. The following explanation appears to me most consistent with the phenomena, though I by no means insist on its accuracy. It is founded on the supposition, or rather, as I conceive, upon the fact, that the nitrous and hyponitrous acids cannot exist alone in water, but are always decomposed by that fluid in consequence of its affinity for nitric acid. When a drop of nitrous acid is added to a very small quantity of water, it is resolved into nitric and hyponitrous acids, the latter being protected from decomposition by the former having combined with the water. The hyponitrous acid is therefore mixed with the solution of nitric acid, or is perhaps chemically united with it. On adding a second portion of nitrous acid, that acid is protected from decomposition by the same circumstance which preserves the hyponitrous; and, consequently, it remains in a state of mixture or combination with the two other acids. If the anhydrous nitrous acid be mixed with a large quantity of water, it is converted into nitric acid and the deutoxide of nitrogen; and every successive addition experiences a similar change, till the water has become sufficiently charged with nitric acid to enable the hyponitrous to exist in it. The subsequent additions of nitrous acid will then be converted into nitric and hyponitrous acids, until the affinity of the water for nitric acid is so far satisfied that it can no longer decompose the nitrous acid.

The changes which are produced in the anhydrous nitrous acid by adding successive portions of water, may be anticipated from what precedes. It is resolved into nitric and hyponitrous acids, and into nitric acid and the deutoxide of nitrogen; and when the dilution is considerable, the greater part, if not the whole, of the hyponitrous acid

will likewise be decomposed. The colour of the fluid at different periods of the process is attributed to the quantity of nitrous acid which is dissolved, and the degree of its dilution. It is difficult however to perceive how an orange coloured liquid should give different shades of green and blue merely by being diluted. May not the blue be caused by the hyponitrous acid, the different shades of green by mixtures of the hyponitrous and nitrous acids, and the yellow and orange by the preponderance of the latter? Some observations of M. Dulong seem to justify this idea, and it is supported by the action of the deutoxide of nitrogen on nitric acid.

Nitrous acid is a powerful oxidizing agent, readily giving oxygen to the more oxidable metals, and to most substances which have a strong affinity for it. The nitrous acid is of course decomposed at the same time; pure nitrogen and the protoxide of nitrogen, are sometimes evolved, but most commonly it is converted into the deutoxide. When transmitted through red-hot porcelain tubes, it suffers decomposition, and a mixture of oxygen and nitrogen gases is obtained.

## *Nitric Acid.*

If a succession of electric sparks be passed through a mixture of oxygen and nitrogen gases confined in a glass tube over mercury, a little water being present, the volume of the gases will gradually diminish, and the water after a time will be found to have acquired acid properties. On neutralizing the solution with potassa, or what is better, by putting a solution of pure potassa instead of water into the tube at the beginning of the experiment, a salt is obtained which possesses all the properties of nitrate of potassa. This experiment was performed in 1785 by Mr. Cavendish, who inferred from it that nitric acid is composed of oxygen and nitrogen. The best proportion of the gases was found to be seven of oxygen to three of nitrogen; but as some nitrous acid is always formed during the process, the exact composition of nitric acid cannot be determined in this way.

Nitric acid may be formed much more conveniently by adding the deutoxide of nitrogen slowly over water to an excess of oxygen gas. Gay-Lussac proved that the nitric acid may in this manner be obtained quite free from the nitrous or hyponitrous acids; and that it is composed of 100 measures of nitrogen, and 250 of oxygen. This result agrees with the proportion which Sir H. Davy has deduced from his observations; and it is confirmed by an analysis of the nitrate of baryta recently made by Dr Henry. Nitric acid is, therefore, composed of

| | *By Volume.* | *By Weight.* | |
|---|---|---|---|
| Nitrogen | 100 | 14 | one equivalent |
| Oxygen | 250 | 40 | five equivalents |

and its combining proportion or equivalent is 54.

Nitric acid cannot exist in an insulated state. The deutoxide of nitrogen and oxygen gases never form nitric acid if mixed together when quite dry; and nitrous acid vapour may be kept in contact with oxygen gas without change, provided no water is present. The most simple form under which chemists have hitherto procured nitric acid is in solution with water; a liquid which, in its concentrated state, is the nitric acid of the pharmacopœia. By manufacturers it is better known by the name of *aqua fortis*.

The nitric acid of commerce is procured by decomposing some salt of nitric acid by means of concentrated sulphuric acid; and common nitre, as the cheapest of the nitrates, is always employed for the pur-

pose. This salt, previously well dried, is put into a glass retort, and a quantity of the strongest sulphuric acid is poured upon it. On applying heat, ebullition ensues, owing to the escape of nitric acid vapours, which must be collected in a receiver kept cold by moist cloths. The heat should be steadily increased during the operation, and continued as long as any acid vapours come over.

Chemists differ as to the best proportions for forming nitric acid. The London College recommends equal weights of nitre and sulphuric acid; and the Edinburgh and Dublin colleges employ three parts of nitre to two of the acid. The proportion of the London College is so calculated, that the potassa of the nitre shall be entirely converted into a bisulphate; for one proportion of nitre (54 nitric acid+48 potassa) is 102, and 98 corresponds to two proportions of concentrated sulphuric acid. To comprehend the nature of this process, it is necessary to observe, that the strong sulphuric acid of commerce consists of one equivalent of dry acid to one of water, and that the strongest nitric acid contains nearly one equivalent of dry or real acid and two equivalents of water. Unless supplied with this proportion of water, the nitric acid is resolved, at the moment of quitting the potassa, into oxygen and nitrous acid. Now in the process of the London College, the water in the oil of vitriol is precisely sufficient for uniting with the nitric acid, and therefore the latter passes over almost entirely as such into the receiver. If the mixture be introduced into the retort without soiling its neck, and the heat cautiously raised, the product will be quite free from sulphuric acid; and therefore the second distillation from nitre, recommended in the pharmacopœia, is superfluous.

The proportions of the Edinburgh and Dublin Colleges are such, that the residual salt is a mixture of the sulphate and bisulphate of potassa. The water of the oil of vitriol, being insufficient for uniting with all the nitric acid, part is decomposed towards the close of the process, and copious red fumes of nitrous acid are disengaged. If the receiver be kept cool, nearly all these vapours are condensed; and the product is a mixture of nitric and nitrous acids, of a deep orange-red colour, very strong and fuming, and of a greater specific gravity, though proportionally less in quantity, than that obtained by the foregoing process. The specific gravity of the pale acid is 1.500, while that of the red acid is 1.520, or by previously drying the nitre and boiling the sulphuric acid, Dr Hope states that it may be made so high as 1.54.

Some manufacturers decompose nitre with half its weight of sulphuric acid, thus employing the ingredients in the proportion of one equivalent of each. In this case about half of the nitric acid is decomposed, and considerable loss sustained, unless the requisite quantity of water is previously mixed with the sulphuric acid, or water placed in the receiver to condense the nitrous acid. Some of the nitre is likewise apt to escape decomposition; and the residue consisting of neutral sulphate, which is much less soluble than the bisulphate, is removed from the retort with difficulty.

In none of the preceding processes, not even in the first, is the product quite colourless; for at the commencement and close of the operation, nitrous acid fumes are disengaged, which communicate a straw-yellow or an orange-red tint, according to their quantity. If a very pale acid is required, two receivers should be used; one for condensing the colourless vapours of nitric acid, and another for the coloured products. The coloured acid is called nitrous acid by the college; but it is in reality a mixture or compound of nitric and nitrous acids, similar to what may be obtained by mixing anhydrous nitrous

with colourless nitric acid. It is easy to convert the common mixed acid of the college into colourless nitric acid, by exposing the former to a gentle heat for some time, when all the nitrous acid will be expelled. But this process is rarely necessary, as the coloured acid may be substituted in almost every case for that which is colourless. Where an acid of great strength is required, the former is even preferable.

Nitric acid frequently contains portions of sulphuric and muriatic acid. The former is derived from the acid which is used in the process; and the latter from sea-salt, which is frequently mixed with nitre. These impurities may be detected by adding a few drops of a solution of muriate of baryta and nitrate of silver to separate portions of nitric acid, diluted with three or four parts of distilled water. If the muriate of baryta cause a cloudiness or precipitate, sulphuric acid must be present; if a similar effect be produced by nitrate of silver, the presence of muriatic acid may be inferred. Nitric acid is purified from sulphuric acid by redistilling it from a small quantity of the nitrate of potassa, with the alkali of which the sulphuric acid unites, and remains in the retort. To separate the muriatic acid, it is necessary to drop a solution of nitrate of silver into the nitric acid as long as a precipitate is formed, and draw off the pure acid by distillation.

Nitric acid possesses acid properties in an eminent degree. A few drops of it diluted with a considerable quantity of water form an acid solution, which reddens litmus paper permanently. It unites with and neutralizes alkaline substances, forming with them salts which are called *nitrates*. In its purest and most concentrated state it is colourless, and has a specific gravity of 1.50 or 1.510. It still contains a considerable quantity of water, from which it cannot be separated without decomposition, or by uniting with some other body. An acid of density 1.50 contains 25 per cent of water, according to the experiments of Mr Phillips; and 20.3 per cent according to those of Dr Ure*. Nitric acid of this strength emits dense, white, suffocating vapours when exposed to the atmosphere. It attracts watery vapour from the air, whereby its specific gravity is diminished. A rise of temperature is occasioned by mixing it with a certain quantity of water. Dr Ure found that when 58 measures of nitric acid, of specific gravity 1.5, are suddenly mixed with 42 of water, the temperature rises from 60 to 140° F. and the mixture on cooling to 60°, occupies the space of 92.65 measures instead of 100. From its strong affinity for water, it occasions snow to liquefy with great rapidity; and an intense degree of cold is generated if the mixture be made in due proportion†.

Nitric acid boils at 248° F. and may be distilled without suffering material change. An acid of less specific gravity than 1.42 becomes stronger by being heated, because the water evaporates more rapidly than the acid. An acid, on the contrary, which is stronger than 1.42 is weakened by the application of heat.

Nitric acid may be frozen by cold. The temperature at which congelation takes place, varies with the strength of the acid. The strongest acid freezes at about 50 degrees below zero. When diluted with half its weight of water, it becomes solid at —1½° F. By the addition of a little more water its freezing point is lowered to —45° F.

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* See his Table in the Appendix, showing the strength of diluted acid of different densities.

† See Table of frigorific mixtures, pages 53 and 54.

Nitric acid acts powerfully on substances which are disposed to unite with oxygen; and hence it is much employed by chemists for bringing bodies to their maximum of oxidation. Nearly all the metals are oxidized by it; and some of them, such as tin, copper, and mercury, are attacked with great violence. If flung on burning charcoal, it increases the brilliancy of its combustion in a high degree. Sulphur and phosphorus are converted into acids by its action. All vegetable substances are decomposed by it. In general the oxygen of the nitric acid enters into direct combination with the hydrogen and carbon of those compounds, forming water with the first, and carbonic acid with the second. This happens remarkably in those compounds in which hydrogen and carbon are predominant, as in alcohol and the oils. It effects the decomposition of animal matters also. The cuticle and nails receive a permanent yellow stain when touched with it; and if applied to the skin in sufficient quantity, it acts as a powerful cautery, destroying the organization of the part entirely.

When oxidation is effected through the medium of nitric acid, the acid itself is commonly converted into the deutoxide of nitrogen. This gas is sometimes given off nearly quite pure; but in general some nitrous acid, protoxide of nitrogen, or pure nitrogen is disengaged at the same time. The direct solar light deoxidizes nitric acid, resolving a portion of it into oxygen and nitrous acid. The former separates; the latter is absorbed by the nitric acid, and converts it into the mixed nitrous acid of the shops. When the vapour of nitric acid is transmitted through red-hot porcelain tubes, it suffers complete decomposition, and a mixture of oxygen and nitrogen gases is the product.

Nitric acid may also be deoxidized by passing a current of the deutoxide of nitrogen through it. That gas, by taking oxygen from the nitric acid, is converted into nitrous acid; and a portion of nitric acid, by losing oxygen, passes into the same compound. The nitrous acid, thus derived, from two sources, gives a colour to the nitric acid the depth and kind of which depend upon the quantity of the deutoxide of nitrogen which has been employed. The first portion communicates a pale straw colour, which gradually deepens as the absorption of the deutoxide continues, till the nitric acid has acquired a deep orange hue, together with all the characters of strong fuming nitrous acid. But the solution still continues to absorb the deutoxide; and in doing so, its colour passes through different shades of olive and green, till it becomes greenish-blue. By applying heat to the blue liquid, the deutoxide of nitrogen is evolved; and in proportion as it escapes, the colour of the solution changes to green, olive, orange, and yellow, at length becoming pale as at first. Nitrous acid vapours are likewise disengaged as well as the deutoxide. These phenomena are very favourable to the view that the conversion of the orange colour into olive, green, and blue, is owing to the formation of hyponitrous acid.

All the salts of nitric acid are soluble in water, and therefore it is impossible to precipitate that acid by any reagent. The presence of nitric acid, when uncombined, is readily detected by its strong action on copper and mercury, and by its forming with potassa a neutral salt, which crystallizes in prisms, and which has all the properties of nitre. Gold leaf is a still more delicate test. When muriatic acid is added to the solution of a nitrate, chlorine is disengaged, and the liquid hence acquires the property of dissolving gold leaf; but as the action of muriatic acid on the salts of chloric and bromic acids likewise

yields a solution capable of dissolving gold, no inference can be drawn from the experiment, except the absence of these acids has been previously demonstrated. A new test of the presence of nitric acid has recently been proposed by Dr Liebig. The liquid to be examined must be mixed with a sufficient quantity of a solution of indigo in sulphuric acid for acquiring a distinct blue colour; a few drops of sulphuric acid must be then added, and the mixture boiled. If a nitrate is present, the liquid will be bleached, or, if the quantity is very small, rendered yellow. By this process nitric acid may be detected, though diluted with 400 times its weight of water; or by adding a little muriate of soda to the liquid before applying heat, 1-500th part of nitric acid may be discovered. (Quarterly Journal of Science for July 1827, p. 204.)

## SECTION VI.

### *CARBON.*

When wood is heated to a certain degree in the open air, it takes fire, and burns with the formation of water and carbonic acid gas, till the whole of it is consumed. A small portion of ashes, consisting of the alkaline and earthy matters which had formed a part of the wood, is the sole residue. But if the wood be heated to redness in close vessels, so that the atmospheric air cannot have free access to it, a large quantity of gaseous and other volatile matters is expelled, and a black, hard, porous substance is left, called *charcoal.*

Charcoal may be procured from other sources. When the volatile matters are driven off from coal, as in the process for making coal gas, a peculiar kind of charcoal, called *coke*, remains in the retort. Most animal and vegetable substances yield it when ignited in close vessels. Thus, a very pure charcoal may be procured from starch or sugar; and from the oil of turpentine or spirit of wine, by passing their vapour through tubes heated to redness. When bones are made red-hot in a covered crucible, a black mass remains, which consists of charcoal mixed with the earthy matters of the bone. It is called *ivory black* or *animal charcoal.*

Charcoal is hard and brittle, conducts heat very slowly, but is a good conductor of electricity. Its density is stated much too low in chemical works:—according to Mr Leslie, its specific gravity is rather greater than that of the diamond. It is quite insoluble in water, is attacked with difficulty by nitric acid, and is little affected by any of the other acids, or by the alkalies. It undergoes little change from exposure to air and moisture, being less injured under these circumstances than wood. It is exceedingly refractory in the fire, if excluded from the air, supporting the most intense heat which chemists are able to produce without change.

Charcoal possesses the property of absorbing a large quantity of air or other gases at common temperatures, and of yielding the greater part of them again when it is heated. It appears from the researches of Saussure, that different gases are absorbed by it in different proportions. His experiments were performed by plunging a piece of red-hot charcoal under mercury, and introducing it when cool into the gas to be absorbed. He found that charcoal prepared from box-wood, absorbs, during the space of 24 or 36 hours, of

| | | |
|---|---|---|
| Ammoniacal gas | . . | 90 times its volume. |
| Muriatic acid | . . | 85 |
| Sulphurous acid | . . | 65 |
| Sulphuretted hydrogen | . . | 55 |
| Nitrous oxide | . . | 40 |
| Carbonic acid | . . | 35 |
| Olefiant gas | . . | 35 |
| Carbonic oxide | . . | 9.42 |
| Oxygen | . . | 9-25 |
| Nitrogen | . . | 7.5 |
| Hydrogen. | . . | 1.75 |

The absorbing power of charcoal with respect to gases, cannot be attributed to chemical action; for the quantity of each gas, which is absorbed, bears no relation whatever to its affinity for charcoal. The effect is in reality owing to the peculiar porous texture of that substance, which enables it, in common with most spongy bodies, to absorb more or less of all gases, vapours, and liquids, with which it is in contact. This property is most remarkable in charcoal prepared from wood, especially in the compact varieties of it, the pores of which are numerous and small. It is materially diminished by reducing the charcoal to powder; and in plumbago, which has not the requisite degree of porosity, it is wanting altogether.

The porous texture of charcoal accounts for the general fact of absorption only; its power of absorbing more of one gas than of another, must be explained on a different principle. This effect, though modified to all appearance by the influence of chemical attraction, seems to depend chiefly on the natural elasticity of the gases. Those which possess such a great degree of elasticity as to have hitherto resisted all attempts to condense them into liquids, are absorbed in the smallest proportion; while those that admit of being converted into liquids by compression, are absorbed more freely. For this reason, charcoal absorbs vapours more easily than gases, and liquids than either.

Messrs Allen and Pepys determined experimentally the increase in weight experienced by different kinds of charcoal, recently ignited, after a week's exposure to the atmosphere. The charcoal from fir gained 13 per cent; that from *lignum vitae*, 9.6; that from box, 14; from beech, 16.3; from oak, 16.5; and from mahogany, 18. The absorption is most rapid during the first 24 hours. The substance absorbed is both water and atmospheric air, which the charcoal retains with such force, that it cannot be completely separated from them without exposure to a red heat. Vogel* has observed that charcoal absorbs oxygen in a much greater proportion from the air than nitrogen. Thus, when recently ignited charcoal, cooled under mercury, was put into a jar of atmospheric air, the residue contained only 8 per cent of oxygen gas; and if red-hot charcoal be plunged into water, and then introduced into a vessel of air, the oxygen disappears almost entirely. It is said that pure nitrogen may be obtained in this way.

Charcoal likewise absorbs the odoriferous and colouring principles of most animal and vegetable substances. When coloured infusions of this kind are digested with a due quantity of charcoal, a solution is obtained, which is nearly if not quite colourless. Tainted flesh may be rendered sweet and eatable by this means, and foul water may be purified by filtering through charcoal. The substance commonly em-

* Schweigger's Journal, vol. iv.

ployed to decolorise fluids is animal charcoal reduced to a fine powder. It loses the property of absorbing colouring matters by use, but recovers it by being heated to redness.

Charcoal is highly combustible. When strongly heated in the open air, it takes fire, and burns slowly. In oxygen gas, its combustion is lively, and accompanied with the emission of sparks. In both cases it is consumed without flame, smoke, or residue, if quite pure; and carbonic acid gas is the product of its combustion.

The pure inflammable principle, which is the characteristic ingredient of all kinds of charcoal, is called *carbon*. In coke it is in a very impure form. Wood-charcoal contains about 1-50th of its weight of alkaline and earthy salts, which constitute the ashes when this species of charcoal is burned. In plumbago, the carbon is combined with a small portion of metallic iron. Charcoal derived from spirit of wine is almost quite pure; and the diamond is carbon in a state of absolute purity.

The diamond is the hardest substance in nature. Its texture is crystalline in a high degree, and its cleavage very perfect. Its primary form is the octahedron. It has a specific gravity of 3.520. Acids and alkalies do not act upon it; and it bears the most intense heat in close vessels without fusing or undergoing any perceptible change. Heated to 14° W, in the open air, it is entirely consumed. Newton first suspected it to be combustible from its great refracting power, a conjecture which was rendered probable by the experiments of the Florentine academicians in 1694, and which was subsequently confirmed by several philosophers. Lavoisier first proved it to contain carbon, by throwing the sun's rays, concentrated by a powerful lens, upon a diamond contained in a vessel of oxygen gas. The diamond was consumed entirely, oxygen disappeared, and carbonic acid was generated. It has since been demonstrated by the researches of Guyton-Morveau, Smithson Tennant, Allen and Pepys, and Sir H. Davy, that carbonic acid is the product of its combustion. Guyton-Morveau inferred from his experiments that the diamond is pure carbon, and that charcoal is an oxide of carbon. Tennant burned diamonds by heating them with nitre in a gold tube; and comparing his own results with those of Lavoisier on the combustion of charcoal, he concluded that equal weights of diamond and pure charcoal, in combining with oxygen, yield precisely equal quantities of carbonic acid. He was thus induced to adopt the opinion, that charcoal and the diamond are chemically the same substance; and that the difference in their physical characters is solely dependent on a difference of aggregation*. This conclusion was confirmed by the experiments of Allen and Pepys†, and Sir H. Davy‡, who compared the product of the combustion of the diamond with that derived from different kinds of charcoal. The latter chemist did indeed observe the production of a minute quantity of water during the combustion of the purest charcoal, indicative of a trace of hydrogen; but its quantity is so exceedingly small, that it cannot be regarded as a necessary constituent. It proves only that a trace of hydrogen is retained with such force by charcoal, that it cannot be expelled by the temperature of ignition.

## *Carbonic Acid.*

Carbonic acid was discovered by Dr. Black in 1757, and described

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* Philos. Trans. for 1797. † Ibid. 1807. ‡ Ibid. 1814.

by him in his inaugural dissertation *de Magnesia Alba*, under the name of *fixed air*. He observed the existence of this gas in common limestone and magnesia, and found that it may be expelled from these substances by the action of heat or acids. He also remarked that the same gas is formed during respiration, fermentation, and combustion. Its composition was first demonstrated synthetically by Lavoisier, who burned carbon in oxygen gas, and obtained carbonic acid as the product. The late Mr Smithson Tennant illustrated its nature analytically by passing the vapour of phosphorus over chalk, or carbonate of lime, heated to redness in a glass tube. The phosphorus took oxygen from the carbonic acid, charcoal in the form of a light black powder was deposited, and the phosphoric acid, which was formed, united with the lime.

Carbonic acid is most conveniently prepared for the purposes of experiment by the action of muriatic acid, diluted with two or three times its weight of water, on fragments of marble. The muriatic acid unites with the lime, forming a muriate of lime, and carbonic acid gas escapes with effervescence.

Carbonic acid, as thus procured, is a colourless, inodorous, elastic fluid, which possesses all the physical characters of the gases in an eminent degree, and requires a pressure of thirty-six atmospheres to condense it into a liquid. According to the recent experiments of Dr Thomson, (First Principles, vol. i. p. 143) 100 cubic inches of it, at 60° F. and when the barometer stands at 30 inches, weigh 46.597 grains; and therefore its specific gravity is 1.5277.

Carbonic acid extinguishes burning substances of all kinds, and the combustion does not cease from the want of oxygen only. It exerts a positive influence in checking combustion, as appears from the fact, that a candle cannot burn in a gaseous mixture composed of four measures of atmospheric air, and one of carbonic acid.

It is not better qualified to support the respiration of animals; for its presence, even in moderate proportion, is soon fatal. An animal cannot live in air which contains sufficient carbonic acid for extinguishing a lighted candle; and hence the practical rule of letting down a burning taper into old wells or pits before any one ventures to descend. When an attempt is made to inspire pure carbonic acid, a violent spasm of the glottis takes place, which prevents the gas from entering the lungs. If it be so much diluted with air as to admit of its passing the glottis, it then acts as a narcotic poison on the system. It is this gas which has often proved destructive to persons sleeping in a confined room with a pan of burning charcoal.

Carbonic acid is quite incombustible, and cannot be made to unite with an additional portion of oxygen. It is a compound, therefore, in which carbon is in its highest degree of oxidation.

Lime-water becomes turbid when brought into contact with carbonic acid. The lime unites with the gas, forming carbonate of lime, which, from its insolubility in water, at first renders the solution milky, and afterwards forms a white flaky precipitate. Hence lime-water is not only a valuable test of the presence of carbonic acid, but is frequently used to withdraw it altogether from any gaseous mixture that contains it.

Carbonic acid is absorbed by water. This may be easily demonstrated, by agitating the gas with that liquid, or by leaving a jar full of it inverted over water. In the first case the gas disappears in the course of a minute; in the latter it is absorbed gradually. Recently boiled water dissolves its own volume of carbonic acid at the common temperature and pressure; but it will take up much more if the pres-

sure be increased. The quantity of the gas absorbed is in exact ratio with the compressing force; that is, water dissolves twice its volume when the pressure is doubled, and three times its volume when the pressure is trebled.

A saturated solution of carbonic acid may be made by passing a stream of the gas through a vessel of cold water during the space of half an hour, or still better by the use of a Woulfe's bottle or Nooth's apparatus, so as to aid the absorption by pressure. Water and other liquids which have been charged with carbonic acid under great pressures, lose the greater part of the gas when the pressure is removed. The effervescence which takes place on opening a bottle of ginger beer, cyder, or brisk champaign, is owing into the escape of carbonic acid gas. Water, which is fully saturated with carbonic acid gas, sparkles when it is poured from one vessel to another. The solution has an agreeably acidulous taste, and gives to litmus paper a red stain which is lost on exposure to the air. On the addition of lime-water to it, a cloudiness is produced, which at first disappears, because the carbonate of lime is soluble in excess of carbonic acid; but a permanent precipitate ensues when the free acid is neutralized by an additional quantity of lime-water. The water which contains carbonic acid in solution is wholly deprived of the gas by boiling. Removal of pressure from its surface by means of the air-pump has a similar effect.

The agreeable pungency of beer, porter, and ale, is in a great measure owing to the presence of carbonic acid, by the loss of which, on exposure to the air, they become stale. All kinds of spring and well water contain carbonic acid absorbed from the atmosphere, and to which they are partly indebted for their pleasant flavour. Boiled water has an insipid taste from the absence of carbonic acid.

A knowledge of the exact composition of carbonic acid gas is of very great importance. The researches of Allen and Pepys, and Sir H. Davy, have proved incontestably that oxygen gas, in combining with carbon so as to form carbonic acid, suffers no change of volume; or, in other words, that carbonic acid contains its own volume of oxygen. It hence follows that 100 cubic inches, or 46.597 grains of carbonic acid, consist of 100 cubic inches, or 33.888 grains of oxygen, united with 12.709 grains (46.597—33.888) of carbon.

$$\text{Now, } 12.709 : 33.888 :: 6 : 16$$

and since, as will soon appear, 6 is the combining proportion of carbon, carbonic acid is composed of

| | | |
|---|---|---|
| Carbon | 6 | one proportional. |
| Oxygen | 16 | two proportionals. |

By a rule which is given at page 129, it may be calculated that carbon, if supposed to exist in the form of vapour, would have a specific gravity of 0.4166; from which it follows, that 100 cubic inches of the vapour of carbon, at 60° F. and when the barometer stands at 30 inches, would weigh 12.709 grains. Consequently, 100 cubic inches of carbonic acid gas are composed of

| | | |
|---|---|---|
| Oxygen gas . | 100 | cubic inches. |
| Vapour of Carbon | 100 | Do. |

Carbonic acid is always present in the atmosphere, even at the summit of the highest mountains, or at a distance of several thousand feet above the ground. Its presence may be demonstrated by exposing lime-water in an open vessel to the air, when its surface will soon be covered with a pellicle, which is carbonate of lime. The origin of the carbonic acid is obvious. Besides being formed abundantly by the combustion of all substances which contain carbon, the respiration of

P 2

animals is a fruitful source of it, as may be proved by breathing for a few minutes into lime-water; and it is also generated in all the spontaneous changes to which dead animal and vegetable matters are subject. The carbonic acid proceeding from such sources, is commonly diffused equably through the air; but when any of these processes occur in low confined situations, as at the bottom of old wells, the gas is then apt to accumulate there, and form an atmosphere called *choke damp*, which is fatal to any animals that are placed in it. These accumulations happily never take place, except when there is some local origin for the carbonic acid; for example, when it is generated by fermentative processes going on at the surface of the ground, or when it issues directly from the earth, as happens at the Grotto del Cane in Italy, and at Pyrmont in Westphalia. There is no real foundation for the opinion that carbonic acid can separate itself from the great mass of the atmosphere, and accumulate in a low situation merely by the force of gravity. Such a supposition is contrary to the well known tendency of gases to diffuse themselves equally through one another. It is also contradicted by observation; for many deep pits, which are free from putrefying organic remains, though otherwise favourably situated for such accumulations, contain good atmospheric air.

Though carbonic acid is the product of many natural operations, chemists have not hitherto noticed any increase in the quantity contained in the atmosphere. The only known process which tends to prevent an increase in its proportion, is that of vegetation. Growing plants purify the air by withdrawing carbonic acid, and yielding an equal volume of pure oxygen in return; but whether a full compensation is produced by this cause, has not yet been satisfactorily determined.

Carbonic acid is contained in the earth. Many mineral springs, such as that of Tunbridge, Pyrmont, and Carlsbad, are highly charged with it. In combination with lime it forms extensive masses of rock, which geologists have found to occur in all countries, and in every formation.

Carbonic acid unites with alkaline substances, and the salts so constituted are called *carbonates*. Its acid properties are feeble, so that it is unable to neutralize completely the alkaline properties of potassa, soda, and lithia. For the same reason, all the carbonates, without exception, are decomposed by the muriatic and all the stronger acids: the carbonic acid is displaced, and escapes in the form of gas.

## *Carbonic Oxide Gas.*

When two parts of well-dried chalk and one of pure iron filings are mixed together, and exposed in a gun-barrel to a red heat, a large quantity of aeriform matter is evolved, which may be collected over water. On examination, it is found to contain two compounds of carbon and oxygen, one of which is carbonic acid, and the other *carbonic oxide*. By washing the mixed gases with lime-water, the carbonic acid is absorbed, and the carbonic oxide gas is left in a state of purity.

A very elegant mode of preparing carbonic oxide has been suggested by M. Dumas. (Edinburgh Journal of Science, No. XII. p. 350.) The process consists in mixing the binoxalate of potassa with five or six times its weight of concentrated sulphuric acid, and heating the mixture in a retort or other convenient glass vessel. Effervescence soon ensues, owing to the escape of gas consisting of equal measures

of carbonic acid and carbonic oxide gases; and on absorbing the former by means of lime-water or solution of potassa, the latter is left in a state of perfect purity. To comprehend the theory of the process, it is necessary to premise, that oxalic acid is a compound of equal measures of carbonic acid and carbonic oxide; or at least its elements are in the proportion to form these gases, and that it cannot exist unless in combination with water or some other substance. Now the sulphuric acid unites both with the potassa and water of the binoxalate, and the oxalic acid being thus set free, is instantly decomposed.

Priestley discovered this gas by igniting chalk in a gun-barrel, and afterwards obtained it in greater quantity from chalk and iron filings. He supposed it to be a mixture of hydrogen and carbonic acid gases. Its real nature was pointed out by Mr Cruickshank*, and about the same time by Clément and Désormes†.

Carbonic oxide gas is colourless and insipid. It does not affect the blue colour of vegetables in any way; nor does it combine, like carbonic acid, with lime or any of the pure alkalies. It is very sparingly dissolved by water. Lime-water does not absorb it, nor is its transparency affected by it.

Carbonic oxide is inflammable. When a lighted taper is plunged into a jar full of that gas, the taper is extinguished; but the gas itself is set on fire, and burns calmly at its surface with a lambent blue flame. The sole product of its combustion, when the gas is quite pure, is carbonic acid, a fact which proves that it does not contain any hydrogen.

Carbonic oxide gas cannot support respiration. It acts injuriously on the system; for if diluted with air, and taken into the lungs, it very soon occasions headach and other unpleasant feelings; and when breathed pure, it almost instantly causes profound coma.

A mixture of carbonic oxide and oxygen gases may be made to explode by flame, by a red-hot solid body, or by the electric spark. If they are mixed together in the proportion of 100 measures of carbonic oxide and rather more than 50 of oxygen, and the mixture is inflamed in Volta's eudiometer by electricity, so as to collect the product of the combustion, the whole of the carbonic oxide, together with 50 measures of oxygen, disappear, and 100 measures of carbonic acid gas occupy their place. From this fact, which was ascertained by Berthollet, and has been amply confirmed by subsequent observation, the exact composition of carbonic oxide gas may be easily deduced. For carbonic acid contains its own bulk of oxygen; and since 100 measures of carbonic oxide with 50 of oxygen form 100 measures of carbonic acid, it follows that 100 of carbonic oxide are composed of 50 of oxygen, united precisely with the same quantity of carbon as is contained in 100 measures of carbonic acid. Consequently, the composition of carbonic acid being

| *By Volume.* | | | *By Weight.* | |
|---|---|---|---|---|
| Vapour of carbon | 100 | | Carbon | 6 |
| | | or | | |
| Oxygen gas | 100 | | Oxygen | 16 |
| | 100 carbonic acid gas. | | | 22 carbonic acid. |

* Nicholson's Journal, 4to Ed. vol v.
† Annales de Chimie, vol. xxxix.

That of carbonic oxide must be

| | *By Volume.* | | *By Weight.* | |
|---|---|---|---|---|
| Vapour of carbon | 100 | or | Carbon | 6 |
| Oxygen gas | 50 | | Oxygen | 8 |
| | 100 carbonic oxide gas. | | | 14 carbonic oxide. |

| | Grains. |
|---|---|
| Also, since 50 cubic inches of oxygen gas weigh | 16.944 |
| and 100 of the vapour of carbon | 12.709 |
| 100 cubic inches of carbonic oxide gas must weigh | 29.653 |

Its specific gravity is therefore 0.9721; and to be satisfied of the accuracy of the data on which these calculations are founded, it is sufficient to state, that its density, as determined by Dr Thomson, is 0.9700, and is 0.9727 according to the experiments of Berzelius and Dulong.

No compound of carbon and oxygen is known which contains a less quantity of oxygen than carbonic oxide. For this reason it is regarded as a combination of one proportion of carbon = 6 and one of oxygen = 8; and carbonic acid, of one proportion of carbon = 6 and two of oxygen = 16. The combining proportion of carbonic oxide is therefore 14, and that of carbonic acid 22.

The first process mentioned for generating carbonic oxide will now be intelligible. The principle of the method is to bring carbonic acid at a red heat in contact with some substance which has a strong affinity for oxygen. This condition is fulfilled by igniting chalk, or any carbonate which can bear a red heat without decomposition, such as the carbonates of baryta, strontia, soda, potassa, or lithia, with half its weight of iron filings or charcoal. The carbonate is reduced to the caustic state, and the carbonic acid is converted into carbonic oxide by yielding oxygen to the iron or the charcoal. When the first is used, an oxide of iron is the product; when charcoal is employed, the charcoal itself is converted into carbonic oxide. This gas may likewise be generated by heating to redness a mixture of almost any metallic oxide with one-sixth of its weight of charcoal powder. The oxides of zinc, iron, or copper, are the cheapest and most convenient. It may also be formed by transmitting a current of carbonic acid gas over ignited charcoal. In all these processes, it is essential that the ingredients be quite free from moisture and hydrogen, otherwise some carburetted hydrogen gas would be generated. The product must always be washed with lime-water to separate it from carbonic acid.

Dr Henry has ascertained that when a succession of electric sparks is passed through carbonic acid confined over mercury, a portion of that gas is converted into carbonic oxide and oxygen. When a mixture of hydrogen and carbonic acid gases is electrified, a portion of the latter yields one half of its oxygen to the former; water is generated, and carbonic oxide produced. On electrifying a mixture of equal measures of carbonic oxide and the protoxide of nitrogen, both gases are decomposed without change of volume, and the residue consists of equal measures of carbonic acid and nitrogen gases. The carbonic oxide should be in very slight excess, in order to ensure the success of the experiment. On this fact is founded Dr Henry's method of analyzing the protoxide of nitrogen, and testing its purity, as will be more particularly mentioned in the fourth part of the work.

# SECTION VII.

## *SULPHUR.*

Sulphur occurs as a mineral production in some parts of the earth, particularly in the neighbourhood of volcanoes, as in Italy and Sicily. It is commonly found in a massive state; but it is sometimes met with crystallized in the form of an oblique rhombic octahedron. It exists much more abundantly in combination with several metals, such as silver, copper, antimony, lead, and iron. It is procured in large quantity by exposing the common iron pyrites to a red heat in close vessels.

Sulphur is a brittle solid, of a greenish-yellow colour, emits a peculiar odour when rubbed, and has little taste. It is a non-conductor of electricity, and is excited negatively by friction. Its specific gravity is 1.99. Its point of fusion is at 216° F; between 230° and 280° it possesses the highest degree of fluidity, is then of an amber colour, and if cast into cylindrical moulds, forms the common roll sulphur of commerce. It begins to thicken near 320°, and acquires a reddish tint; and at temperatures between 428° and 482°, it is so tenacious that the vessel may be inverted without causing it to change its place. From 482° to its boiling point it becomes liquid again, but never to the same extent as when at 248°. When heated to at least 428°, and then poured into water, it becomes a ductile mass, which may be used for taking the impression of seals. (Dumas.)

Fused sulphur has a tendency to crystallize in cooling. A crystalline arrangement is perceptible in the centre of the common roll sulphur; and by good management regular crystals may be obtained. For this purpose, several pounds of sulphur should be melted in an earthern crucible; and when partially cooled, the outer solid crust should be pierced, and the crucible quickly inverted, so that the inner and as yet fluid parts may gradually flow out. On breaking the solid mass, when quite cold, crystals of sulphur will be found in its interior.

Sulphur is very volatile. It begins to rise slowly in vapour even before it is completely fused. At 550° or 600° F. it volatilizes rapidly, and condenses again unchanged in close vessels. Common sulphur is purified by this process; and if the sublimation be conducted slowly, the sulphur collects in the receiver in the form of detached crystalline grains, called *flowers of sulphur*. In this state, however, it is not quite pure; for the oxygen of the air within the apparatus combines with a portion of sulphur during the process, and forms sulphurous acid. The acid may be removed by washing the flowers repeatedly with water.

Sulphur is insoluble in water, but unites with it under favourable circumstances, forming the white *hydrate of sulphur*, termed *Lac Sulphuris*. It dissolves readily in boiling oil of turpentine. The solution has a reddish-brown colour like melted sulphur, and if fully saturated deposites numerous small crystals in cooling. Sulphur is also soluble in alcohol, if both substances are brought together in the form of vapour. The sulphur is precipitated from the solution by the addition of water.

Sulphur, like charcoal, retains a portion of hydrogen so obstinately that it cannot be wholly freed from it either by fusion or sublimation.

Sir H. Davy detected its presence by exposing sulphur to the strong heat of a powerful galvanic battery, when some sulphuretted hydrogen gas was disengaged. The hydrogen, from its minute quantity, can only be regarded in the light of an accidental impurity, and as nowise essential to the nature of sulphur.

When sulphur is heated in the open air to 300° F. or a little higher, it kindles spontaneously, and burns with a faint blue light. In oxygen gas its combustion is far more vivid; the flame is much larger, and of a bluish-white colour. Sulphurous acid is the product in both instances;—no sulphuric acid is formed even in oxygen gas unless moisture is present.

## *Compounds of Sulphur and Oxygen.*

Chemists are at present acquainted with four compounds of sulphur and oxygen, all of which have acid properties. Their composition is shown by the following table.

| | *Sulphur.* | *Oxygen.* | | *Pr.S.* | *Pr.Ox.* |
|---|---|---|---|---|---|
| Hyposulphurous acid | 32 | 8 | . | 2 | 1 |
| Sulphurous acid | 16 | 16 | . | 1 | 2 |
| Sulphuric acid | 16 | 24 | . | 1 | 3 |
| Hyposulphuric acid | 32 | 40 | . | 2 | 5 |

## *Sulphurous Acid Gas.*

Pure sulphurous acid, at the common temperature and pressure, is a colourless transparent gas, which was first obtained in a separate state by Priestley*. It is the sole product when sulphur is burned in air or dry oxygen gas, and is the cause of the peculiar odour emitted by that substance during its combustion. It may also be prepared by depriving sulphuric acid of one proportion of its oxygen. This may be done in several ways. If chips of wood, straw, or cork, oil, or other vegetable matters, be heated in strong sulphuric acid, the carbon and hydrogen of those substances deprive the acid of part of its oxygen, and convert it into sulphurous acid. Nearly all the metals, with the aid of heat, have a similar effect. One portion of sulphuric acid yields oxygen to the metal, and is thereby converted into sulphurous acid; while the metallic oxide, at the moment of its formation, unites with some of the undecomposed sulphuric acid. The best method of obtaining pure sulphurous acid gas, is by putting two parts of mercury and three of sulphuric acid into a glass retort, the beak of which is received under mercury, and heating the mixture by an Argand lamp. Effervescence soon takes place, a large quantity of pure sulphurous acid is disengaged, and the sulphate of the oxide of mercury remains in the retort.

Sulphurous acid gas is distinguished from all other gaseous fluids by its suffocating pungent odour. All burning bodies, when immersed in it, are extinguished without setting fire to the gas itself. It is fatal to all animals which are placed in it. A violent spasm of the glottis takes place, by which the entrance of the gas into the lungs is prevented; and even when diluted with air, it excites cough, and causes a peculiar uneasiness about the chest.

Recently boiled water dissolves about 33 times its volume of sul-

* Priestley on Air, vol. ii. p. 1.

phurous acid, at 60° F. and 30 inches of the barometer, forming a solution which has the peculiar odour of that compound, and from which the gas may be expelled by ebullition, without change.

Sulphurous acid has considerable bleaching properties. It reddens litmus paper, and then slowly bleaches it. Most vegetable colouring matters, such as that of the rose and the violet, are speedily removed, without being first reddened by it. It is remarkable that the colouring principle is not destroyed by the sulphurous acid; it may be restored either by a stronger acid or by an alkali.

Sir H. Davy inferred from his experiments on the combustion of sulphur in dry oxygen gas, (Elements, p. 273,) that the volume of the oxygen is not altered during the process, a fact which is now admitted by most chemists; so that 100 cubic inches of sulphurous acid contain 100 cubic inches of oxygen. According to Dr Thomson, (Annals of Philosophy, xvi. 256,) sulphurous acid gas is just twice as heavy as oxygen; and the experiments of Davy and of Thenard correspond very closely with his result. It follows, therefore, that sulphurous acid consists of equal weights of sulphur and oxygen; and consequently that 100 cubic inches weigh 67.776 grains, and contain 33.888 grains of sulphur. This proportion is also established by the researches of Berzelius. (An. de Ch. et de Ph. vol. v.)

By the formula, page 129, it may be calculated that the specific gravity of the vapour of sulphur is the same as that of oxygen gas, or 1.1111; and hence 100 cubic inches of that vapour must weigh 33.888 grains. From this it is manifest, that 100 cubic inches of sulphurous acid gas are composed of

| | |
|---|---|
| Vapour of sulphur . . | 100 cubic inches. |
| Oxygen . . . | 100 do. |

The specific gravity of sulphurous acid gas is of course double that of oxygen, or 2.2222.

It is inferred from the compounds of sulphur with oxygen, hydrogen, and many other substances, that 16 is the number which expresses the combining proportion of that substance. Hence sulphurous acid is composed of 16, or one proportion of sulphur, and 16, or two proportions of oxygen. Its atomic weight is, therefore, 32.

Though sulphurous acid cannot be made to burn by the approach of flame, it has a very strong attraction for oxygen, uniting with it under favourable circumstances, and forming sulphuric acid. The presence of moisture is essential to this change. A mixture of sulphurous acid and oxygen gases, if quite dry, may be preserved over mercury for any length of time without acting on each other. But if a little water be admitted, the sulphurous acid gradually unites with oxygen, and disappears entirely. For this reason, a solution of sulphurous acid in water cannot be kept unless the atmospheric air is carefully excluded. Many of the chemical properties of sulphurous acid are owing to its affinity for oxygen. On being added to a solution of the peroxide of iron, it takes oxygen, and thus converts the peroxide into the protoxide of that metal. The solutions of metals which have a weak affinity for oxygen, such as gold, platinum, and mercury, are completely decomposed by it, those substances being precipitated in the metallic form. Nitric acid converts it instantly into sulphuric acid, by yielding some of its oxygen. The peroxide of manganese causes a similar change, and is itself converted into the protoxide of manganese, which unites with the sulphuric acid.

Sulphurous acid gas may be passed through red-hot tubes without decomposition. Several substances which have a strong affinity for

oxygen, such as hydrogen, carbon, and potassium, decompose it at the temperature of ignition.

Of all the gases, sulphurous acid is most readily liquefied by compression. According to Mr Faraday, it is condensed by a force equal to the pressure of two atmospheres. M. Bussy (Annals of Phil. viii. 307, N.S.) has obtained it in a liquid form under the usual atmospheric pressure, by passing it through tubes surrounded by a freezing mixture of snow and salt. The anhydrous liquid acid has a density of 1.45. It boils at 14° F. From the rapidity of its evaporation at common temperatures, it may be used advantageously for producing an intense degree of cold. M. Bussy succeeded in freezing mercury, and liquefying several of the gases, by the cold produced during its evaporation.

Sulphurous acid combines with metallic oxides, and forms salts which are called *sulphites*.

## *Sulphuric Acid.*

Sulphuric acid, or *oil of vitriol* as it is often called, was discovered by Basil Valentine towards the close of the 15th century. It is procured for the purposes of commerce by two methods. The first is the process which has been pursued many years in the manufactory at Nordhausen in Germany, and consists in decomposing the sulphate of the protoxide of iron (green vitriol) by heat. The crystallized protosulphate of iron contains seven proportionals of water of crystallization; and when strongly dried by the fire, it crumbles down into a white powder, which, according to Dr Thomson, contains one proportional of water. On exposing this dried protosulphate of iron to a red heat, the whole of the sulphuric acid is expelled, the greater part of it passing over unchanged into the receiver, in combination with the water of the salt. One proportion of the acid is resolved by the strong heat employed in the distillation into sulphurous acid and oxygen. The former escapes as gas throughout the whole process; the latter only in the middle and latter stages, being retained, in the beginning of the distillation, by the protoxide of iron. The peroxide of iron is the sole residue.

The acid, as procured by this process, is a dense, oily liquid of a brownish tint. It emits copious white vapours on exposure to the air, and is hence called *fuming sulphuric acid*. Its specific gravity is stated at 1.896 and 1.90.

From the analysis of Dr Thomson, it is composed of.

| | | |
|---|---|---|
| Anhydrous sulphuric acid . | 80 . | two proportions. |
| Water . | 9 . | one proportion. |

On putting this acid into a glass retort, to which a receiver surrounded by snow is securely adapted, and applying a very gentle heat to it, a transparent colourless vapour passes over, which condenses into a white crystalline solid. This substance is shown by the experiments of Thomson, Ure, and Bussy, to be pure anhydrous sulphuric acid. It is tough and elastic, liquefies at 66° F. and boils at a temperature between 104° and 122°, forming, if no moisture is present, a transparent vapour. Exposed to the air, it unites with watery vapour, and flies off in the form of dense white fumes. The residue of the distillation is no longer fuming, and is in every respect similar to the common acid of commerce.

The second process for forming sulphuric acid, which is practised in Britain and in most parts of the Continent, is by burning sulphur pre-

viously mixed with one-eighth of its weight of nitrate of potassa. The mixture is burned in a furnace so contrived that the current of air which supports the combustion, conducts the gaseous products into a large leaden chamber, the bottom of which is covered to the depth of several inches with water. The nitric acid yields oxygen to a portion of sulphur, and converts it into sulphuric acid, which combines with the potassa of the nitre; while the greater part of the sulphur forms sulphurous acid by uniting with the oxygen of the air. The nitric acid, in losing oxygen, is converted into the deutoxide of nitrogen, which, by mixing with air at the moment of its separation, gives rise to the red nitrous acid vapours. The gaseous substances present in the leaden chamber, are, therefore, sulphurous and nitrous acids, atmospheric air, and watery vapour. The explanation of the mode in which these substances react on one another, so as to form sulphuric acid, was suggested by Clement and Desormes, (An. de Ch. vol. lix.) and the subject has been put in a still clearer light by Sir H. Davy. (Elements, p. 276.) On mixing together dry sulphurous acid gas and nitrous acid vapour in a glass vessel quite free from moisture, no change ensues; but if a drop of water be added, so as to fill the space with vapour, a white crystalline solid is formed, which is composed of water and the two acids. When these crystals come into contact with water, the sulphurous acid takes oxygen from the nitrous acid, the deutoxide of nitrogen escapes with effervescence, and the sulphuric acid is dissolved by the water.

A similar change takes place within the leaden chamber. The crystalline solid is decomposed by the water at the bottom of the chamber, by which sulphuric acid is generated, and the deutoxide of nitrogen set free. That gas, in mixing with atmospheric air, is again converted into nitrous acid, and thus gives rise to the formation of a second portion of the crystalline solid, which is resolved, like the preceding, into sulphuric acid and the deutoxide of nitrogen. These successive combinations and decompositions continue till the water is sufficiently charged with sulphuric acid, when it is drawn off and concentrated by evaporation.

It hence appears that the oxygen by which the sulphurous is converted into sulphuric acid, is in reality supplied by the air; and that the combination is effected, not directly, but through the medium of the nitrous acid. The decomposition of the crystalline solid by water seems owing to the affinity of the water for sulphuric acid.

Sulphuric acid, as thus prepared, is never quite pure. It contains some sulphate of potassa and of lead, the former derived from the nitre employed in making it, the latter from the leaden chamber. To separate these impurities, the acid should be distilled from a glass or platinum retort. The former may be used with safety by putting some fragments of platinum leaf into it, which causes the acid to boil freely on the application of heat without danger of breaking the vessel.

Pure sulphuric acid, as obtained by the second process, is a dense, colourless, oily fluid, which boils at 620° F, and has a specific gravity, in its most concentrated form, of 1.847 or a little higher, never exceeding 1.850. It is one of the strongest acids with which chemists are acquainted. When undiluted it is powerfully corrosive. It decomposes all animal and vegetable substances by the aid of heat, causing deposition of charcoal and formation of water. It has a strong sour taste, and reddens litmus paper, even though greatly diluted. It unites with alkaline substances, and separates all other acids more or less completely from their combinations with the alkalies.

Sulphuric acid has a very great affinity for water, and unites with it

in every proportion. The combination takes place with the production of intense heat. When four parts by weight of the acid are suddenly mixed with one of water, the temperature of the mixture rises, according to Dr Ure, to 300° F. By its attraction for water it causes the sudden liquefaction of snow; and if mixed with it in due proportion, (p. 53,) an intense degree of cold is generated. It absorbs watery vapour with avidity from the air, and on this account is employed in the process for freezing water by its own evaporation. The operation of sulphuric acid in destroying the texture of the skin, in forming ethers, and in decomposing animal and vegetable substances in general, seems dependent on its affinity for water.

The sulphuric acid of commerce freezes at —15° F. Diluted with water so as to have a specific gravity of 1.78, it congeals even above 32°, and remains in the solid state, according to Mr Keir, till the temperature rises to 45°. When mixed with rather more than its weight of water, its freezing point is lowered to —36° F.

When sulphuric acid is passed through a small porcelain tube heated to redness, it is entirely decomposed; and Gay-Lussac found that it is resolved into two measures of sulphurous acid and one of oxygen. Hence it follows that real sulphuric acid is composed of

| *By Weight.* | | | | *By Volume.* | |
|---|---|---|---|---|---|
| Sulphur . | 16 | one p. | or | Vapour of sulphur | 100 |
| Oxygen . | 24 | three p. | | Oxygen gas . | 150 |

and its atomic weight is 40. Berzelius ascertained its composition by converting a known weight of sulphur into sulphuric acid; and his result confirms the conclusion of Gay-Lussac.

Chemists possess an unerring test of the presence of sulphuric acid. If a solution of muriate of baryta is added to a liquid containing sulphuric acid, it causes a white precipitate, the sulphate of baryta, which is characterized by its insolubility in acids and alkalies.

Sulphuric acid does not occur free in nature, except occasionally in the neighbourhood of volcanoes. In combination, particularly with lime and baryta, it is very abundant.

*Hyposulphurous acid.*—This acid may be formed either by digesting sulphur in a solution of any sulphite; or by passing a current of sulphurous acid into a solution of the hydrosulphuret of lime or strontia. In the first case, the sulphurous acid takes up an additional quantity of sulphur, and a salt of hyposulphurous acid is obtained; and in the second, the sulphurous acid is deprived of one-half of its oxygen by the hydrogen of the sulphuretted hydrogen, while the other half of the oxygen unites both with the sulphur of the sulphurous acid and of the sulphuretted hydrogen, to form hyposulphurous acid. If the hydrosulphuret of lime employed contains bisulphuretted hydrogen, as is the case when lime and sulphur are boiled together, the action of sulphurous acid is accompanied by precipitation of sulphur. Mr Herschel states that hyposulphurous acid may be formed by the action of sulphurous acid on iron filings; but the nature of the change is not well understood.

The salts of hyposulphurous acid were first described by Gay-Lussac in the 85th volume of the *Annales de Chimie*, under the name of *Sulphuretted Sulphites*. Dr Thomson in his System of Chemistry suggested that the acid of these salts might be regarded as a compound of one equivalent of sulphur and one of oxygen, and proposed for it the name of *hyposulphurous* acid. The subsequent researches of Mr Herschel (Edinburgh Philos. Journal, i. 8 and 396) seemed to give such direct analytic proof of the correctness of this opinion, that it was

universally adopted; but it appears from a very recent essay by Dr Thomson, that this view of its composition is nevertheless erroneous, and that the acid consists of 32 parts or two equivalents of sulphur, and 8 parts or one equivalent of oxygen. Its combining proportion is, therefore, 40. (On the Compounds of Chromium, Philos. Trans. for 1827.)

Hyposulphurous acid cannot exist permanently in a free state. On decomposing a hyposulphite by any stronger acid, such as the sulphuric or muriatic, the hyposulphurous acid, at the moment of quitting the base, resolves itself into sulphurous acid and sulphur. Mr Herschel succeeded in obtaining free hyposulphurous acid, by adding a slight excess of sulphuric acid to a dilute solution of the hyposulphite of strontia; but its decomposition very soon took place, even at common temperatures, and was instantly effected by heat. Most of the hyposulphites are soluble in water, and have a bitter taste. The solution precipitates the nitrate of silver and mercury black, as the sulphuret of the metals; and salts of lead and baryta are thrown down as white insoluble hyposulphites of those bases. That of baryta is soluble without decomposition in water acidulated with muriatic acid. The solution of all the neutral hyposulphites has the peculiar property of dissolving recently precipitated chloride of silver in large quantity, and forming with it a liquid of an exceedingly sweet taste.

Dr Thomson, in the essay above quoted, mentions that an acid exists composed of one equivalent of sulphur and one of oxygen; but he has given no description of it.

*Hyposulphuric Acid.*—The hyposulphuric acid was discovered in 1819 by Welter and Gay-Lussac, who published their description of it in the 10th vol. of the *Ann. de Ch. et de Physique*. It is formed by passing a current of sulphurous acid gas through water containing peroxide of manganese in fine powder. The manganese yields oxygen to the sulphurous acid, converting one part of it into sulphuric, and another part into the hyposulphuric acid, both of which unite with the protoxide of manganese. To the liquid, after filtration, a solution of pure baryta is added in slight excess, which precipitates the protoxide of manganese, and forms an insoluble sulphate of baryta with the sulphuric, and a soluble hyposulphate with the hyposulphuric acid. The hyposulphate of baryta is then decomposed by a quantity of sulphuric acid exactly sufficient for precipitating the baryta, and the hyposulphuric acid is left in solution.

This compound reddens litmus paper, has a sour taste, and forms neutral salts with the alkalies. It has no odour, by which circumstance it is distinguished from sulphurous acid. It cannot be confounded with the sulphuric acid; for it forms soluble salts with baryta, strontia, lime, and the oxide of lead, whereas the compounds which sulphuric acid forms with those bases are all insoluble. The hyposulphuric acid cannot be obtained free from water. Its solution, if confined with a vessel of sulphuric acid under the exhausted receiver of an air-pump, may be concentrated till it has a density of 1.347; but if an attempt is made to condense it still further, the acid is decomposed, sulphurous acid gas escapes, and sulphuric acid remains in solution. A similar change is still more readily produced, if the evaporation is conducted by heat.

Welter and Gay-Lussac analyzed the hyposulphuric acid by applying heat to the neutral hyposulphate of baryta. At a temperature a little above 212° F. this salt suffers complete decomposition; sulphurous acid gas is disengaged, and a neutral sulphate of baryta is obtained. They ascertained in this way, that seventy-two grains of hypo-

sulphuric acid yield thirty-two grains of sulphurous, and forty of sulphuric acid; from which it is inferred that the hyposulphuric acid is composed either of an equivalent of each of those acids, combined directly with one another, or of two equivalents of sulphur, and five of oxygen. Regarded as a definite compound of sulphur and oxygen, its composition is,

| | | | |
|---|---|---|---|
| Sulphur | . . | 32 | two proportionals. |
| Oxygen | . . | 40 | five proportionals. |
| | | 72 | |

Its combining proportion, whichever opinion is adopted, is 72.

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## SECTION VIII.

### *PHOSPHORUS.*

Phosphorus was discovered about the year 1669 by Brandt, an alchemist of Hamburgh. It was originally prepared from urine; but Scheele afterwards described a method of obtaining it from bones. The object of both processes is to bring phosphoric acid in contact with charcoal at a strong red heat. The charcoal takes oxygen from the phosphoric acid; carbonic acid is disengaged, and phosphorus set free. When urine is employed, the phosphoric acid contained in it should be separated by a solution of the acetate of lead. The phosphate of lead subsides, which, if heated to redness with one-fourth of its weight of powdered charcoal, yields phosphorus readily. If bones are to be used, they should first be ignited in an open fire till they become quite white, so as to destroy all the animal matter they contain, and oxidize the carbon proceeding from its decomposition. The calcined bones, of which phosphate of lime constitutes nearly four-fifths, should be reduced to fine powder, and digested for a day or two with half their weight of concentrated sulphuric acid, so much water being added to the mixture as to give it the consistence of thin paste. The phosphate of lime is decomposed by the sulphuric acid, and two new salts are generated,—the sparingly soluble neutral sulphate, and a soluble super-phosphate of lime. On the addition of boiling water the super-phosphate is dissolved, and may be separated by filtration from the sulphate of lime. The solution is then evaporated to the thickness of syrup, mixed with one-fourth of its weight of charcoal in powder, and heated in an earthen retort well luted with clay. The beak of the retort is put into water, in which the phosphorus, as it passes over in the form of vapour, is collected. When first obtained, it is frequently of a reddish-brown colour, owing to the presence of phosphuret of carbon, which is generally formed during the process. It may be purified by being put into hot water, and pressed while liquid through chamois leather; or the purification may be rendered still more complete by a second distillation.

Pure phosphorus is transparent and almost colourless. It is so soft that it may be cut with a knife, and the cut surface has a waxy lustre. At the temperature of 108° F. it fuses, and at 550° is converted into vapour. It is soluble by the aid of heat in naphtha, in fixed and volatile oils, and in the chloride, carburet, and phosphuret of sulphur. On cooling from its solution in the latter, Professor Mitscherlich obtained it in regular dodecahedral crystals. By the fusion and slow

cooling of a large quantity of phosphorus, M. Frantween has obtained very fine crystals of an octahedral form, and as large as a cherry-stone.

Phosphorus is exceedingly inflammable. Exposed to the air at common temperatures, it undergoes a slow combustion; emits a white vapour of a peculiar alliaceous odour, appears distinctly luminous in the dark, and is gradually consumed. On this account, phosphorus should always be kept under water. The disappearance of oxygen which accompanies these changes is shown by putting a stick of phosphorus in a jar full of air, inverted over water. The volume of the gas gradually diminishes, and if the temperature of the air is at 60, F. the whole of the oxygen will be withdrawn in the course of 12 or 24 hours. The residue is nitrogen gas, containing about 1-40th of its bulk of the vapour of phosphorus. It is remarkable that the slow combustion of phosphorus does not take place in pure oxygen, unless its temperature be about 80°. But if the oxygen is diluted with nitrogen, hydrogen, or carbonic acid gas, the oxidation occurs at 60°; and it takes place at temperatures still lower in a vessel of pure oxygen, rarefied by diminished pressure*. I have been favoured with the

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* If a stick of dry phosphorus be dusted over with powdered resin or sulphur, and then introduced under the receiver of an air-pump, it will be found that, as soon as the exhaustion commences, the phosphorus will become luminous, which appearance increases as the rarefaction proceeds, until finally the phosphorus inflames. Van Bemmelen, who first attempted to account for this phenomenon, attributes it to the combination of the sulphur or resin with the phosphorus, the union of which, accelerated by the influence of the vacuum, gives rise to the evolution of so much heat, as to inflame the phosphorus, or the new compound formed. Berzelius rejects this explanation, as it does not account for an experiment by Van Bemmelen, in which phosphorus was found to take fire under an exhausted receiver, when merely enveloped with cotton. *Berzelius, Traité de Chimie*, i. 260.

Professor A. D. Bache, of the University of Pennsylvania, has repeated and extended the experiments of Van Bemmelen, and has had the goodness to communicate to me an abstract of his results, which are as follows:—

Professor Bache succeeded in producing the inflammation of the phosphorus, under the circumstances above mentioned, by means of the following substances in a finely divided state, in addition to those employed by Van Bemmelen:—

| | |
|---|---|
| Carbon, in the form of ivory black and wood-charcoal. | Lime. |
| Spongy platinum. | Peroxide of manganese. |
| Antimony. | Hydrate of potassa. |
| Arsenic. | Muriate of ammonia. |
| Bisulphuret of mercury. | Chloride of Sodium. |
| Sulphuret of antimony. | Fluate of lime. |
| Silica. | Carbonate of lime. |

Sulphur and charcoal were the substances which succeeded most readily. With metallic arsenic there was much difficulty. The temperature of the room has great influence on the success of the experiments.

Professor Bache is of opinion that some of his experiments are unfavourable to the explanation of Van Bemmelen; as for example, those with carbonate of lime and fluor spar, which, though incombustible substances, act with the same energy as sulphur or carbon. B.

following curious facts by Mr Graham, who is at present occupied with the investigation of this subject. He finds that the presence of certain gaseous substances, even in minute quantity, have a remarkable effect in preventing the slow combustion of phosphorus. Thus at 66° F. it is entirely prevented by the presence of

| | *Volumes of air.* |
|---|---|
| 1 volume of olefiant gas in | 450 |
| 1 ditto of vapour of sulphuric ether in | 150 |
| 1 ditto of vapour of naphtha in | 1820 |
| 1 ditto of vapour of oil of turpentine in | 4444 |

and by an equally slight impregnation of the vapour of the other essential oils. Their influence is not confined to low temperatures. Phosphorus becomes faintly luminous in the dark, in mixtures of

| | | |
|---|---|---|
| 1 volume of air | and 1 volume of olefiant gas at | 200° F. |
| 1 . . | and 1 ditto of vapour of ether at | 215° |
| 11 . . | and 1 ditto of vapour of naphtha at | 170° |
| 166 . . | and 1 ditto of vapour of turpentine at | 186° |

Phosphorus may be sublimed at its boiling temperature in air containing a considerable proportion of the vapour of oil of turpentine, without diminishing the quantity of oxygen present, provided the heat is gradually and uniformly applied. Mr Graham has also remarked, that the oxidation of phosphorus in air is promoted by the presence of muriatic acid gas.

A very slight degree of heat is sufficient to inflame phosphorus in the open air. Gentle pressure between the fingers, friction, or a temperature not much above its point of fusion, kindles it readily. It burns rapidly even in the air, emitting a splendid white light, and causing intense heat. Its combustion is far more rapid in oxygen gas, and the light proportionably more vivid.

## *Compounds of Phosphorus and Oxygen.—Phosphoric Acid.*

Of the compounds of phosphorus and oxygen, *phosphoric acid* is by far the most interesting and important. This acid may be obtained in a state of perfect purity by burning phosphorus in air or oxygen gas. Copious white vapours are produced, which fall to the bottom of the vessel like flakes of snow. In this state it is the solid anhydrous phosphoric acid. From its powerful affinity to water, it attracts watery vapour rapidly from the atmosphere, and in the course of two or three minutes appears in the form of minute drops of liquid, which is a solution of phosphoric acid in water.

Phosphoric acid may be conveniently formed by the action of nitric acid on phosphorus. The phosphorus takes oxygen from the nitric acid, and a large quantity of deutoxide of nitrogen is disengaged; but as the reaction is apt to be very violent, the process ought to be conducted with caution. It is best done by adding fragments of phosphorus to concentrated nitric acid contained in a platinum capsule. Gentle heat is applied so as to commence, and, when necessary, to maintain moderate effervescence; and when one portion of phosphorus disappears, another is added, till the whole of the nitric acid is exhausted. The solution is then evaporated to dryness, and exposed to a red heat to expel the last traces of nitric acid. The last part of this process must be performed in vessels of platinum, since phosphoric acid acts chemically upon those of glass or porcelain, and is thereby rendered impure.

Phosphoric acid may be prepared at a much cheaper rate from bones. For this purpose, the super-phosphate of lime, obtained in the way already described, should be boiled for a few minutes with excess of the carbonate of ammonia. The lime is thus precipitated as a carbonate*, and the solution contains phosphate, together with a little sulphate, of ammonia. The liquid, after filtration, is evaporated to dryness, and then ignited in a platinum crucible, by which the ammonia and sulphuric acid are expelled.

Solid phosphoric acid unites with water in every proportion, and forms, if concentrated, a dense oily liquid. On heating the solution in a platinum vessel, the greater part of the water is driven off; the residue fuses at a low red heat, and concretes on cooling into a brittle glass, called *glacial phosphoric acid*. This substance is a hydrate of phosphoric acid, which cannot be decomposed by the fire; for on exposing it to a strong red heat, with the view of expelling the water, the compound itself is volatilized, and in open vessels sublimes with considerable rapidity. It is erroneously said to be fixed at intense degrees of heat, this character applying to the acid only in its impure state, as when combined with earthy or alkaline substances. The composition of the glacial phosphoric acid is not yet established; for while M. Dulong reports it to contain 17.08 per cent of water, M. Rose found only 9.44 per cent. (Poggendorff's Annalen, VIII. 201.) The analysis of Rose, though not rigidly exact, is I suspect not far from the truth. The acid after being fused in glass vessels is anhydrous.

Phosphoric acid is intensely sour to the taste, reddens litmus paper strongly, and neutralizes alkalies. It is, therefore, a powerful acid; but it does not destroy the texture of the skin like sulphuric and nitric acids. It may be distinguished from all other acids by the following circumstances:—that when carefully neutralized by pure carbonate of soda or potassa, it forms a solution in which no precipitate or change of colour is produced when a stream of sulphuretted hydrogen gas is passed through it; but which is precipitated white by a solution of the acetate of lead, and yellow by the nitrate of silver. The first precipitate, the phosphate of lead, dissolves completely on the addition of nitric or phosphoric acid; the second, the phosphate of silver, is dissolved by both these acids, and also by ammonia.

The composition of phosphoric acid has been investigated by Sir H. Davy, Dr Thomson, Berzelius, and M. Dulong. The subject is one of much difficulty, and the results of the two former chemists differ widely from those of the two latter. Dr Thomson infers† from experiments made by Sir H. Davy and himself, (and his estimate is generally adopted in this country), that 28 is the combining proportion of phosphoric acid, and that it consists of 12 parts, or what he considers one equivalent of phosphorus, and 16 parts or two equivalents of oxygen. A variety of circumstances, however, which it is not material to mention at present, induce me to doubt the accuracy of Dr Thomson's experiments on this subject; and I shall therefore adopt the results of Berzelius as preferable. According to the researches of this chemist, as well as of M. Dulong, the oxygen contained in the phosphorous and phosphoric acids is in the ratio of 1.5 to 2.5, or 3 to

* Dr. Turner is inaccurate here. The ammonia neutralizes the excess of phosphoric acid, the carbonic acid is evolved, and the lime precipitates as a neutral phosphate. B.

† First Principles, vol. i. p. 203.

5; and the former states phosphoric acid to consist of 56 parts of oxygen and 44 of phosphorus. Now, judging from the composition of the phosphates, analyzed by Berzelius and Mitscherlich, and from the data just mentioned, we may regard 35.71 as the combining proportion of phosphoric acid, and this acid itself as a compound of 15.71 parts or one proportion of phosphorus, and 20 parts or two equivalents and a half of oxygen. Berzelius considers this acid as a compound of two atoms of phosphorus and five atoms of oxygen, and therefore doubles the preceding numbers*.

*Phosphorous Acid.*—When phosphorus is heated in highly rarefied air, imperfect oxidation ensues, and the phosphoric and phosphorous acids are both generated, the latter being obtained in the form of a white volatile powder. In this state it is anhydrous. Heated in the open air, it takes fire, and forms phosphoric acid; but if exposed to heat in close vessels, it is resolved into phosphoric acid and phosphorus. It dissolves readily in water, has a sour taste, and smells somewhat like garlic. It unites with alkalies, and forms salts which are termed *phosphites*. The solution of phosphorous acid absorbs oxygen slowly from the air, and is converted into phosphoric acid. From its tendency to unite with an additional quantity of oxygen, it is a powerful deoxidizing agent; and, hence, like sulphurous acid, precipitates mercury, silver, platinum, and gold, from their saline combinations in the metallic form. Nitric acid, of course, converts it into phosphoric acid.

Phosphorous acid may be procured more conveniently by subliming phosphorus through powdered corrosive sublimate, (a compound of

* Considering the uncertainty in which the composition of the acids of phosphorus is still involved, it is to be regretted that Dr Turner has thought proper to adopt the analytic results of Berzelius and Dulong respecting these compounds, which has the effect of giving a new equivalent number for phosphorus, and a different view of the number of equivalents found in them. As the subject cannot yet be considered as decided, it would have been better to wait until further researches had finally settled the question of their composition, rather than hastily reject the numbers, which have heretofore been almost universally adopted by the British and American chemists. It deserves to be mentioned that the composition of phosphoric acid, as given by Dr Thomson, which coincides nearly with the analysis of Sir H. Davy, is not materially different from the results of Berzelius, who states it to be 56 parts of oxygen and 44 of phosphorus. Now the proportions of 16 parts of oxygen and 12 of phosphorus will give in the 100 parts, 57.1 parts of oxygen and 42.9 parts of phosphorus. This is a virtual agreement in the analysis of this acid, and, therefore, the discrepancy relates to its saline equivalent. Berzelius finds this to be 35.71, and Dr Thomson believes it to be 28. The difficulty certainly rests here, and it must be acknowledged that there is a strong probability that Berzelius's number is correct; as it is not easy to see how he could be mistaken in his analyses of the phosphates. Still it appears inexpedient to abandon the numbers generally received, with a view to adopt others, which cannot yet be considered as fully established. The substitution in this case is peculiarly unfortunate, as it admits a fractional number to represent phosphorus, and adopts fractional equivalents for the oxygen both of phosphorous and phosphoric acids. It ought to be a strong case of analytic proof that would justify the author in adopting numbers so little in accordance with the laws of combination. B.

chlorine and mercury,) contained in a glass tube*. A limpid liquid comes over which is a compound of chlorine and phosphorus. When this substance is put into water, a peculiar change occurs. A portion of water is decomposed; its hydrogen unites with the chlorine, and forms muriatic acid; while the oxygen attaches itself to the phosphorus, by which phosphorous acid is produced. The solution is then evaporated to the consistence of syrup to expel the muriatic acid; and the residue, which is the hydrate of phosphorous acid, becomes a crystalline solid on cooling. On heating this hydrate in close vessels, the elements of the water and acid react on each other, forming phosphoric acid and a gaseous compound of hydrogen and phosphorus. The nature of this gas will be more particularly noticed in the section on phosphuretted hydrogen.

Phosphorous acid is also generated during the slow oxidation of phosphorus in atmospheric air. The product attracts moisture from the air, and forms an oily-like liquid. M. Dulong thinks that a distinct acid is generated in this case, which he calls *phosphatic acid*; but the opinion of Sir H. Davy, that it is merely a mixture of phosphoric and phosphorous acids is, I conceive, correct.

The composition of the phosphorous, like that of phosphoric acid, is not yet satisfactorily ascertained. Sir H. Davy and Dr Thomson consider the oxygen in the two acids as 1 to 2, while according to Dulong and Berzelius the proportion is as 3 to 5.

*Hypophosphorous Acid.*—This acid was discovered in 1816 by M. Dulong†, and is produced by the action of water on the phosphuret of baryta. The water suffers decomposition; its elements unite with different portions of phosphorus, by which three compounds, phosphuretted hydrogen, phosphoric acid, and hypophosphorous acid, are generated. The first escapes in the form of gas; and the two latter combine with the baryta. The hypophosphite of baryta, being soluble, dissolves in the water, and may consequently be separated by filtration from the phosphate of baryta, which is insoluble. On adding a sufficient quantity of sulphuric acid for precipitating the baryta, the hypophosphorous acid is obtained in a free state. On evaporating the solution, a viscid liquid remains, highly acid and even crystallizable, which is a *hydrate of hypophosphorous acid*. When exposed to heat in close vessels it undergoes the same kind of change as hydrated phosphorous acid.

The hypophosphorous acid is a powerful deoxidizing agent. It unites with alkaline bases; and it is remarkable that all its salts are soluble in water. The hypophosphites of potassa, soda, and ammonia, dissolve in every proportion in rectified alcohol; and the hypophosphite of potassa is even more deliquescent than chloride of calcium. They are all decomposed by heat, and yield the same products as the acid itself.

M. Dulong determined the proportion of its elements by converting it into phosphoric acid by means of chlorine. He infers from his analysis that it contains 27.25 per cent of oxygen. According to Sir H. Davy, it has exactly one half less oxygen than the phosphorous acid; but as the composition of this acid is not known with certainty, no inference can be safely deduced from the statement. Professor Henry Rose states that it contains 20.31 per cent of oxygen, so that its elements are in the ratio of 31.42 parts or two proportionals of

* Davy's Elements, p. 288.

† Mem. d'Arcueil, vol. iii. or An. de Ch. et de Physique, vol. ii.

phosphorus, and 8 parts or one proportional of oxygen. (Poggendorff's Annalen, IX. 367). From this discordance it may be inferred that the chemical constitution of the hypophosphorous acid, like that of the other acids of phosphorus, is at present involved in much obscurity.

*Oxides of Phosphorus.*—Chemists have not yet succeeded in proving the existence of any oxide of phosphorus. When phosphorus is kept under water for some time, a white film is formed upon its surface, which some have regarded as an oxide of phosphorus. The red-coloured matter which remains after the combustion of phosphorus, is also supposed to be an oxide. The nature of these substances has not, however, been determined in a satisfactory manner.

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## SECTION IX.

### *BORON.*

Sir H. Davy discovered the existence of *Boron* in 1807, by exposing boracic acid to the action of a powerful galvanic battery; but he did not obtain a sufficient supply of it for determining its properties. It was procured in greater quantity by Gay-Lussac and Thenard* in 1808, by heating boracic acid with potassium. The boracic acid is by this means deprived of its oxygen, and boron is set free. The easiest and most economical method of preparing this substance, according to Berzelius, is to decompose an alkaline borofluate by means of potassium. (Annals of Philosophy xxvi. 128.)

Boron is a dark olive-coloured substance, which has neither taste nor smell, and is a non-conductor of electricity. It is insoluble in water, alcohol, ether, and oils. It does not decompose water whether hot or cold. It bears an intense heat in close vessels, without fusing or undergoing any other change, except a slight increase of density. Its specific gravity is about twice as great as that of water. It may be exposed to the atmosphere at common temperatures without change; but if heated to 600° F. it suddenly takes fire, oxygen gas disappears, and boracic acid is generated. It experiences a similar change when heated in nitric acid, or with any substance that yields oxygen with facility.

*Boracic acid.* This is the only known compound of boron and oxygen. As a natural product it is found in the hot springs of Lipari, and in those of Sasso in the Florentine territory. It is a constituent of several minerals, among which the datolite and boracite may in particular be mentioned. It occurs much more abundantly under the form of borax, a native compound of boracic acid and soda. It is prepared for chemical purposes by adding sulphuric acid to a solution of purified borax in about four times its weight of boiling water, till the liquid acquires a distinct acid reaction. The sulphuric acid unites with the soda; and the boracic acid is deposited, when the solution cools, in a confused group of shining scaly crystals. It is then thrown on a filter, washed with cold water to separate the adhering

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* Recherches Physico-Chimiques, vol. i.

sulphate of soda and sulphuric acid, and still further purified by solution in boiling water and re-crystallization. But even after this treatment it is apt to retain a little sulphuric acid, and on this account, when required to be absolutely pure, should be fused in a platinum crucible, and once more dissolved in hot water and crystallized.

Boracic acid in this state is a hydrate. Its precise degree of solubility in water has not been determined with accuracy; but it is much more soluble in hot than in cold water. Boiling alcohol dissolves it freely, and the solution, when set on fire, burns with a beautiful green flame; a test which affords the surest indication of the presence of boracic acid. Its specific gravity is 1.479. It has no odour, and its taste is rather bitter than acid. It reddens litmus paper feebly, and effervesces with alkaline carbonates. Mr Faraday has noticed that it renders turmeric paper brown like the alkalies. From the weakness of its acid properties, all the borates, when in solution, are decomposed by the stronger acids.

When hydrous boracic acid is exposed to a gradually increasing heat in a platinum crucible, its water of crystallization is wholly expelled, and a fused mass remains which bears a white heat without being sublimed. On cooling, it forms a hard, colourless, transparent glass, which is anhydrous boracic acid. If the water of crystallization be driven off by the sudden application of a strong heat, a large quantity of boracic acid is carried away during the rapid escape of watery vapour. The same happens, though in a less degree, when a solution of boracic acid in water is boiled briskly. Vitrified boracic acid should be preserved in well stopped vessels; for if exposed to the air, it absorbs water, and gradually loses its transparency. Its specific gravity is 1.803. It is exceedingly fusible, and communicates this property to the substances with which it unites. For this reason borax is often used as a flux.

The most obvious mode of determining the composition of boracic acid is to burn a known quantity of boron, and ascertain its increase of weight when the combustion ceases. This method, however, though apparently simple, is very difficult of execution; for the boracic acid fuses at the moment of being generated, and by glazing the surface of the unconsumed boron, protects it from oxidation. Hence it was that the experiments performed by Gay-Lussac and Thenard on this subject, led to results widely different from those which Sir H. Davy obtained by a similar process. Dr Thomson, from data furnished partly by himself, and partly by Sir H. Davy, infers that the atomic weight of boron is 8, and that boracic acid is composed of

| | |
|---|---|
| Boron . . | 8, or one equivalent. |
| Oxygen . . | 16, or two equivalents. |

Consequently, the equivalent of boracic acid is 24.

Crystallized boracic acid, according to the same chemist, is composed of

| | |
|---|---|
| Boracic acid . | 24, or one equivalent. |
| Water . . | 18, or two equivalents. |
| and therefore its equivalent is | 42. |

*Sulphuret of Boron.*—This compound may be formed according to Berzelius, by igniting boron strongly in the vapour of sulphur, and the combination is accompanied with the phenomena of combustion. The product is a white opake mass, which is converted by the action of water into sulphuretted hydrogen and boracic acid; and the liquid becomes milky at the same time from a deposition of sulphur. (Annals of Philosophy, xxvi. 129.)

# SECTION X.

## *SELENIUM.*

Selenium has hitherto been found in very small quantity. It occurs for the most part in combination with sulphur in some kinds of iron pyrites. Stromeyer has also detected it, as a sulphuret of selenium, among the volcanic products of the Lipari isles. It is found likewise at Clausthal, in the Hartz mountains, combined, according to Stromeyer and Rose, with several metals, such as lead, cobalt, silver, mercury, and copper. It was discovered in 1818 by Berzelius in the sulphur obtained by sublimation from the iron pyrites of Fahlun. In a manufactory of sulphuric acid at which this sulphur was employed, it was observed that a reddish-coloured matter always collected at the bottom of the leaden chamber; and on burning this substance, Berzelius perceived a strong and peculiar odour, similar to that of decayed horse-radish, which induced him to submit it to a careful examination, and thus led to the discovery of selenium*.

Selenium, at common temperatures, is a brittle opake solid body, without taste or odour. It has a metallic lustre and the aspect of lead, when in mass; but is of a deep red colour when reduced to powder. Its specific gravity is between 4.3 and 4.32. At 212° it softens, and is then so tenacious that it may be drawn out into fine threads which are transparent, and appear red by transmitted light. It becomes quite fluid at a temperature somewhat above that of boiling water. It boils at about 650°, forming a vapour which has a deep yellow colour, but emitting no odour. It may be sublimed in close vessels without change, and condenses again into dark globules of a metallic lustre, or as a cinnabar-red powder, according as the space in which it collects is small or large. Berzelius at first regarded it as a metal; but, since it is an imperfect conductor of caloric and electricity, it more properly belongs to the class of the simple non-metallic bodies.

Selenium is insoluble in water. It suffers no change from mere exposure to the atmosphere; but if heated in the open air, it combines readily with oxygen, and two compounds, the oxide of selenium and selenious acid, are generated. If the experiment is made by throwing upon it the oxidizing part of the blow-pipe flame, it tinges the flame of a light blue colour, and exhales so strong an odour of decayed horse-radish, that 1-50th of a grain is said to be sufficient to scent the air of a large apartment. By this character the presence of selenium, whether alone or in combination, may always be detected.

*Oxide of Selenium.*—This compound is formed in greatest abundance by heating selenium in a limited quantity of atmospheric air, and washing the product to separate the selenious acid. It is a colourless gas, which is very sparingly soluble in water, and does not possess any acid properties. It is the cause of the peculiar odour which is emitted during the oxidation of selenium. Its composition has not been determined, but it probably contains an atom of each of its elements.

*Selenious Acid*—This acid is most conveniently prepared by digesting selenium in nitric or nitro-muriatic acid till it is completely dis-

* An. de Ch. et de Phys. vol. ix., or Annals of Philosophy, vol. xiii.

solved. On evaporating the solution to dryness, a white residue is left, which is selenious acid. By increase of temperature, the acid itself sublimes, and condenses again unchanged into long four-sided needles. It attracts moisture from the air, whereby it suffers imperfect liquefaction. It dissolves in alcohol and water. It has distinct acid properties, and its salts are called *selenites.*

Selenious acid is readily decomposed by all substances which have a strong affinity for oxygen, such as sulphurous and phosphorous acids. When sulphurous acid, or an alkaline sulphite, is added to a solution of selenious acid, a red-coloured powder, pure selenium, is thrown down, and the sulphurous converted into sulphuric acid. Sulphuretted hydrogen also decomposes it; and an orange-yellow precipitate subsides, which is a sulphuret of selenium.

The atomic weight of selenium, deduced chiefly from the experiments of Berzelius, is 40; and the selenious acid, according to the analysis of the same chemist, consists of

| | | |
|---|---|---|
| Selenium | 40 | one equivalent. |
| Oxygen | 16 | two equivalents. |
| | 56 | |

*Selenic acid.*—The preceding compound, discovered by Berzelius, was till lately the only known acid of selenium, and has hitherto been described in elementary works under the name of selenic acid; but the recent discovery of another acid of selenium containing more oxygen than the other, has rendered necessary a change of nomenclature. The existence of the selenic acid was first noticed by M. Nitzsch, assistant of Professor Mitscherlich, and its properties have been examined and described by the professor himself. (Edin. Journal of Science, No. XVI. 294.)

This acid is prepared by fusing nitrate of potassa or soda with selenium, a metallic seleniuret, or with selenious acid or any of its salts. The seleniuret of lead, as the most common ore of selenium, will generally be employed; but it is very difficult to obtain pure selenic acid by its means, because it is commonly associated with metallic sulphurets. The ore is first treated with muriatic acid to remove any carbonate that may be present; and the insoluble part, which is about a third of the mass, is mixed with its own weight of nitrate of soda, and thrown by successive portions into a red-hot crucible. The lead is thus oxidized, and the selenium converted into selenic acid, which unites with soda. The fused mass is then acted on by hot water, which dissolves only the seleniate of soda, together with nitrate and nitrite of soda; while the insoluble matter, when well washed, is quite free from selenium. The solution is next made to boil briskly, when anhydrous seleniate of soda is deposited; while on cooling nitrate of soda crystallizes. On renewing the ebullition and subsequent cooling, fresh portions of the seleniate and nitrate are procured; and these successive operations are repeated, until the former salt is entirely separated. This process is founded on the fact, that seleniate of soda, like the sulphate of the same base, is more soluble in water of about 90° F. than at higher or lower temperatures. The nitrite of soda, formed during the fusion, is purposely reconverted into nitrate by digestion with nitric acid.

The seleniate of soda thus procured always contains a little sulphuric acid, derived from the metallic sulphurets of the ore; and it is not possible to separate this acid by crystallization. All attempts to separate it by means of baryta were likewise fruitless; and the only method of effecting this object is by reducing the selenic acid into selenium. This is done by heating a mixture of the seleniate of soda and

sal ammoniac; when mutual decomposition ensues, the soda unites with muriatic acid, the hydrogen of the ammonia combines with the oxygen of the selenic acid, and selenium and nitrogen are set free. The selenium thus obtained is quite free from sulphur. It is then converted by nitric acid into selenious acid, neutralized with soda, the seleniate generated by fusion with nitre or nitrate of soda, and separated according to the foregoing process. The pure seleniate of soda is subsequently dissolved in water, and obtained in crystals by spontaneous evaporation.

To procure the acid in a free state, the seleniate of soda is decomposed by nitrate of lead. The seleniate of lead, which is as insoluble as the sulphate, after being well washed, is exposed to a current of sulphuretted hydrogen gas, which precipitates all the lead as a sulphuret, but does not decompose the selenic acid. The excess of sulphuretted hydrogen is driven off by heat, and pure selenic acid remains diluted with water. The absence of fixed substances may be proved by its being volatilized by heat without residue; and if free from sulphuric acid, it gives no precipitate with muriate of baryta after being boiled with muriatic acid*. Any nitric acid which may be present is expelled by concentrating the solution by means of heat.

Selenic acid is a colourless liquid, which may be heated to 536° F. without appreciable decomposition; but above that point decomposition commences, and becomes rapid at 554° giving rise to disengagement of oxygen and selenious acid. When concentrated by a temperature of 329° its specific gravity is 2.524; at 512° it is 2.60, and at 545° it is 2.625, but a little selenious acid is then present. When procured by the process above described, selenic acid always contains water, but it is very difficult to ascertain its precise proportion. Some acid which had been heated higher than 536°, contained, subtracting the quantity of selenious acid present, 15.75 per cent of water, which approximates to the ratio of one equivalent of water and one of the acid. It is certain that selenic acid is decomposed by heat before parting with all the water which it contains.

Selenic acid has a powerful affinity for water, and emits as much heat in uniting with it as sulphuric acid does. Like this acid it is not decomposed by sulphuretted hydrogen, and hence this gas may be employed for decomposing the seleniate of lead or copper. With muriatic acid the change is peculiar; for on boiling the mixture, mutual decomposition ensues, water and selenious acid are formed, and chlorine set free; so that the solution, like *aqua regia*, is capable of dissolving gold and platinum. Selenic acid dissolves zinc and iron with disengagement of hydrogen gas, and copper with formation of selenious acid. It dissolves gold also, but not platinum. Sulphurous acid has no action on selenic acid, whereas selenious acid is easily reduced by it. Consequently, when it is wished to precipitate selenium from selenic acid, it must be boiled with muriatic acid before sulphurous acid is added.

Selenic acid, in its affinity for alkaline bases, is little inferior to sulphuric acid; so much so, indeed, that the seleniate of baryta cannot be completely decomposed by sulphuric acid. It is therefore an acid of great power. From the analysis of this acid and of the seleniates

* The necessity of this previous boiling with muriatic acid is to convert the selenic into selenious acid, without which change the muriate of baryta would produce a precipitate of seleniate of baryta. The rationale of the action of muriatic acid is explained further on. B.

of potassa and soda by professor Mitscherlich, it is established that the oxygen of the selenious and selenic acids, combined with the same quantity of selenium, is in the ratio of 2 to 3, as is the case with sulphurous and sulphuric acids. Hence the selenic acid is a compound of 40 parts, or one equivalent of selenium, and 24 parts, or three equivalents of oxygen; and its equivalent is 64.

Professor Mitscherlich has observed, that the selenic and sulphuric acids are not only analogous in composition and many of their properties, but that the similarity runs through their compounds with alkaline substances, their salts resembling each other in chemical properties, constitution, and form.

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## SECTION XI.

### *CHLORINE.*

The discovery of chlorine was made in the year 1770 by Scheele while investigating the nature of manganese, and he described it under the name of *dephlogisticated marine acid.* The French chemists called it *oxygenized muriatic acid*, a term which was afterwards contracted to *oxy-muriatic acid*, from an opinion proposed by Berthollet that it is a compound of muriatic acid and oxygen. In 1809 Gay-Lussac and Thenard published an abstract of some experiments upon this substance, which subsequently appeared at length in their *Recherches Physico-Chimiques*, wherein they stated that oxymuriatic acid might be regarded as a simple body, though they gave the preference to the doctrine advanced by Berthollet. Sir H. Davy engaged in the inquiry about the same time, and after having exposed oxymuriatic acid to the most powerful decomposing agents which chemists possess, without being able to effect its decomposition, he communicated to the Royal Society an essay, in which he denied its compound nature, and maintained that, according to the true logic of chemistry, it is entitled to rank with simple bodies. This view, which is commonly termed the *new theory of chlorine*, though strongly objected to at the time it was first proposed, is now almost universally received by chemists, and accordingly is adopted in this work. The grounds of preference will hereafter be briefly stated.

Chlorine gas is obtained by the action of muriatic acid on the peroxide of manganese. The most convenient method of preparing it is by mixing concentrated muriatic acid, contained in a glass flask, with half its weight of finely powdered peroxide of manganese. Effervescence, owing to the escape of chlorine, takes place even in the cold; but the gas is evolved much more freely by the application of a moderate heat. It should be collected in inverted glass bottles filled with warm water; and when the water is wholly displaced by the gas, the bottles should be closed with a well-ground glass stopper. As some muriatic acid gas commonly passes over with it, the chlorine should not be considered quite pure, till after being transmitted through water.

Before explaining the theory of this process, it may be premised that muriatic acid consists of 36 parts or one equivalent of chlorine, and 1 part or one equivalent of hydrogen. The peroxide of manganese, as already mentioned, (page 135,) is composed of 28 parts or one equivalent of manganese, and 16 or two equivalents of oxygen. When

[illegible] compounds react on one another, one equivalent of each is [illegible]. The peroxide of manganese gives one equivalent of oxygen to the hydrogen of the muriatic acid, in consequence of which one equivalent of water is generated, and one equivalent of chlorine [illegible]; while the protoxide of manganese unites with an equivalent of undecomposed muriatic acid, and forms an equivalent of [illegible] of the protoxide of manganese. Consequently, for every [illegible] of the peroxide of manganese, 74 (37×2) grains of real muriatic acid [illegible]; and 36 parts of chlorine, 9 of water, and 73 [illegible] of manganese, are the products of the decomposition. The [illegible] which determine these changes are the attraction [illegible] hydrogen, and of the protoxide of manganese for muriatic acid.

[illegible] object to prepare chlorine at the cheapest rate, as [illegible] manufacture, the preceding process is modified in [illegible]. Three parts of sea-salt are intimately mixed [illegible] of the peroxide of manganese, and to this mixture two parts [illegible] acid, diluted with an equal weight of water, are then [illegible]. By the action of sulphuric acid on sea-salt muriatic acid is [illegible], which reacts as in the former case upon the peroxide of manganese [illegible]. Instead of adding muriatic acid directly to the [illegible] the materials for forming it are employed. In this process [illegible] the protoxide of manganese unites with sulphuric [illegible], and the residue is sulphate of manganese and [illegible].

[illegible] is a yellowish-green coloured gas, which has an astringent [illegible]. It is one of the most suffocating [illegible] irritation of the glottis, even [illegible]. When strongly and suddenly [illegible], a character which it possesses [illegible]. According to Sir H. Davy, 100 cubic [illegible] stands at 30 inches, [illegible]. Dr Thomson states its weight at [illegible] with that of Gay-Lussac [illegible] specific gravity is 2.5. [illegible] It is a limpid liquid of a [illegible] at the temperature of [illegible] with the appearance of [illegible]

[illegible] absorbs twice [illegible]. The solution [illegible] gas through [illegible] properties of the [illegible] of 32° F. [illegible] water and chlorine in [illegible] to Mr Faraday, [illegible]

the hydrogen to form muriatic acid, and oxygen gas is set at liberty. This change takes place quickly in sunshine, more slowly in diffused day-light, and not at all when the light is wholly excluded. Hence the necessity of keeping moist chlorine gas, or its solution, in a dark place, if it is wished to preserve it for any time.

Chlorine unites with some substances with evolution of heat and light, and is hence termed a supporter of combustion. If a lighted taper be plunged into chlorine gas, it burns for a short time with a small red flame, and emits a large quantity of smoke. Phosphorus takes fire in it spontaneously, and burns with a pale white light. Several of the metals, such as tin, copper, arsenic, antimony, and zinc, when introduced into chlorine in the state of powder or in fine leaves, are suddenly inflamed. In all these cases the combustible substances unite with chlorine.

Chlorine has a very powerful attraction for hydrogen; and many of the chemical phenomena to which chlorine gives rise, are owing to this property. A striking example is its power of decomposing water by the action of light, or at a red heat; and most compound substances, of which hydrogen is an element, are deprived of that principle, and therefore decomposed in like manner. For the same reason, when chlorine, water, and some other body which has a strong affinity for oxygen, are presented to one another, the water is usually resolved into its elements, the hydrogen attaches itself to the chlorine, and the oxygen to the other body. Hence it happens that chloiine is indirectly one of the most powerful oxidizing agents which we possess.

When any compound of chlorine and an inflammable is exposed to the influence of galvanism, the inflammable body goes over to the negative, and the chlorine to the positive pole of the battery. This establishes a close analogy between oxygen and chlorine, both of them being supporters of combustion, and both negative electrics.

Chlorine, though formerly called an acid, possesses no acid properties. It has not a sour taste, does not redden the blue colour of plants, and shows comparatively little disposition to unite with alkalies. Its strong affinity for the metals is sufficient to prove that it is not an acid; for chemists are not acquainted with any instance of an acid combining directly in definite proportion with a metal.

The mutual action of chlorine and the pure alkalies leads to complicated changes. If chlorine gas is passed into a solution of potassa till all alkaline reaction ceases, a liquid is obtained which has the odour of a solution of chlorine in water. But on applying heat, the chlorine disappears entirely, and the solution is found to contain two neutral salts, the chlorate and muriate of potassa. The production of the two acids is owing to the decomposition of water, the elements of which unite with separate portions of chlorine, and form the chloric and muriatic acids. The affinities which give rise to this change, are the attraction of chlorine for hydrogen, of chlorine for oxygen, and of the two resulting acids for the alkali.

One of the most important properties of chlorine is its bleaching [illegible]er. All animal and [illegible]urs are speedily removed by [illegible]ine; and when th[illegible] [illegible]lischarged, it can never be [illegible]ed. Sir H. Dav[illegible] [illegible]rine cannot bleach unless [illegible] present. Thu[illegible] [illegible] suffers no change in dry [illegible] but when wa[illegible] [illegible]olour speedily disappears. [illegible]known also, [illegible] always generated when [illegible]aches. Fro[illegible] [illegible]nferred that water is de[illegible] the proce[illegible] [illegible]n unites with chlorine, [illegible]mposition of [illegible]atter is occasioned by

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When it is an object to prepare chlorine at the cheapest rate, as for the purposes of manufacture, the preceding process is modified in the following manner. Three parts of sea-salt are intimately mixed with one of the peroxide of manganese, and to this mixture two parts of sulphuric acid, diluted with an equal weight of water, are then added. By the action of sulphuric acid on sea-salt muriatic acid is disengaged, which reacts as in the former case upon the peroxide of manganese; so that, instead of adding muriatic acid directly to the manganese, the materials for forming it are employed. In this process, however, the protoxide of manganese unites with sulphuric instead of muriatic acid, and the residue is sulphate of manganese and sulphate of soda.

Chlorine* is a yellowish-green coloured gas, which has an astringent taste, and a disagreeable odour. It is one of the most suffocating of the gases, exciting spasm and great irritation of the glottis, even when considerably diluted with air. When strongly and suddenly compressed, it emits both heat and light, a character which it possesses in common with oxygen gas. According to Sir H. Davy, 100 cubic inches of it at 60° F. and when the barometer stands at 30 inches, weigh between 76 and 77 grains. Dr Thomson states its weight at 76.25 grains, and his result agrees very nearly with that of Gay-Lussac and Thenard. Adopting this estimate, its specific gravity is 2.5. Under the pressure of about four atmospheres it is a limpid liquid of a bright yellow colour, which does not freeze at the temperature of zero, and which assumes the gaseous form with the appearance of ebullition when the pressure is removed.

Cold recently boiled water, at the common pressure, absorbs twice its volume of chlorine, and yields it again when heated. The solution, which is made by transmitting a current of chlorine gas through cold water, has the colour, taste, and most of the other properties of the gas itself. When moist chlorine gas is exposed to a cold of 32° F. yellow crystals are formed, which consist of water and chlorine in definite proportions. They are composed, according to Mr Faraday, of 36 or one equivalent of chlorine to 90 or ten equivalents of water.

Chlorine experiences no chemical change from the action of the imponderables. Thus it is not affected chemically by intense heat, by strong shocks of electricity, or by a powerful galvanic battery. Sir H. Davy exposed it also to the action of charcoal heated to whiteness by galvanic electricity, without separating oxygen from it, or in any way affecting its nature. Light does not act on dry chlorine; but f water be present, the chlorine decomposes that liquid, unites with

* From χλωρος, green.

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Chlorine, though formerly called an acid, possesses no acid properties. It has not a sour taste, does not redden the blue colour of plants, and shows comparatively little disposition to unite with alkalies. Its strong affinity for the metals is sufficient to prove that it is not an acid; for chemists are not acquainted with any instance of an acid combining directly in definite proportion with a metal.

The mutual action of chlorine and the pure alkalies leads to complicated changes. If chlorine gas is passed into a solution of potassa till all alkaline reaction ceases, a liquid is obtained which has the odour of a solution of chlorine in water. But on applying heat, the chlorine disappears entirely, and the solution is found to contain two neutral salts, the chlorate and muriate of potassa. The production of the two acids is owing to the decomposition of water, the elements of which unite with separate portions of chlorine, and form the chloric and muriatic acids. The affinities which give rise to this change, are the attraction of chlorine for hydrogen, of chlorine for oxygen, and of the two resulting acids for the alkali.

One of the most important properties of chlorine is its bleaching power. All animal and vegetable colours are speedily removed by chlorine; and when the colour is once discharged, it can never be restored. Sir H. Davy proved that chlorine cannot bleach unless water is present. Thus, dry litmus paper suffers no change in dry chlorine; but when water is admitted, the colour speedily disappears. It is well known also, that muriatic acid is always generated when chlorine bleaches. From these facts it is inferred that water is decomposed during the process, that its hydrogen unites with chlorine, and that the decomposition of the colouring matter is occasioned by

R 2

the oxygen which is liberated. The bleaching property of the deutoxide of hydrogen, of which oxygen is certainly the decolorizing principle, leaves little doubt of the accuracy of the foregoing explanation.

Chlorine is useful, likewise, for the purposes of fumigation. The experience of Guyton-Morveau is sufficient evidence of its power in destroying the volatile principles given off by putrefying animal matter; and it probably acts in a similar way on contagious effluvia. A peculiar compound of chlorine and soda, the nature of which will be considered in the section on Sodium, has been lately introduced for this purpose by M. Labarraque.

Chlorine is in general easily recognized by its colour and odour. Chemically it may be detected by its bleaching property, added to the circumstance that a solution of the nitrate of silver occasions in it a dense white precipitate (a compound of chlorine and metallic silver), which becomes dark on exposure to light, is insoluble in acids, and dissolves completely in pure ammonia. The whole of the chlorine, however, is not thrown down by nitrate of silver; for the oxygen of the oxide of silver unites with a portion of chlorine, and converts it into chloric acid.

The compounds of chlorine, which are not acid, are termed *chlorides* or *chlorurets*. The former expression is perhaps the more appropriate, from the analogy between chlorine and oxygen.

## *Compound of Chlorine and Hydrogen.—Muriatic Acid Gas*.*

*Muriatic or hydrochloric acid gas* was discovered by Priestley in 1772. It may be conveniently prepared by putting an ounce of the strong muriatic acid of the pharmacopoeia into a glass flask, and heating it by means of a lamp till the liquid boils. Pure muriatic acid gas is freely evolved, and may be collected over mercury. Another method of preparing it is by the action of concentrated sulphuric acid on an equal weight of sea-salt. Brisk effervescence ensues at the moment of making the mixture, and on the application of heat a large quantity of muriatic acid gas is disengaged. In the first process, muriatic acid, previously dissolved in water, is simply expelled from the solution by increased temperature. The explanation of the second process is rather more complicated. Sea-salt was formerly supposed to be a compound of muriatic acid and soda; and, on this supposition, the soda was believed merely to quit the muriatic and unite with sulphuric acid. But according to the experiments of Gay-Lussac and Thenard and Sir H. Davy, sea-salt in its dry state consists, not of muriatic acid and soda, but of chlorine and sodium, the metallic base of soda. The proportion of its constituents are

| | | |
|---|---|---|
| Chlorine | 36 | one proportional. |
| Sodium | 24 | one proportional. |

When sulphuric acid is added to it, one proportion of water is resolved into its elements; the hydrogen unites with chlorine, forming

* I have here deviated slightly from my arrangement. I have done so, because it will facilitate the study of the compounds of chlorine with the simple non-metallic bodies, to describe them in the same section. Iodine and bromine, for a like reason, will be treated in a similar manner.

muriatic acid, which escapes in the form of gas; while soda is generated by the combination of the oxygen with sodium, which combines with the sulphuric acid, and forms sulphate of soda. The water contained in the liquid sulphuric acid is therefore essential to the success of the operation. The affinities which determine the change are the attraction of chlorine for hydrogen, of sodium for oxygen, and of soda for sulphuric acid.

Muriatic acid may be generated by the direct union of its elements. When equal measures of chlorine and hydrogen are mixed together, and an electric spark is passed through the mixture, instantaneous combination takes place, heat and light are emitted, and muriatic acid is generated. A similar effect is produced by flame, by a red-hot body, and by spongy platinum. Light also causes them to unite. A mixture of the two gases may be preserved without change in a dark place; but if exposed to the diffused light of day, gradual combination ensues, and is completed in the course of 24 hours. The direct solar rays produce, like flame or electricity, sudden inflammation of the whole mixture, accompanied with explosion; and according to Mr Brande, the vivid light emitted by charcoal intensely heated by galvanic electricity acts in a similar manner.

The experiments of Davy, and Gay-Lussac and Thenard concur in proving that hydrogen and chlorine unite in equal volumes, and that the muriatic acid which is the sole and constant product, occupies the same space as the gases from which it is formed. From these facts the composition of muriatic acid is easily inferred. For, as

| | | *Grains.* |
|---|---|---|
| 50 cubic inches of chlorine weigh | . | 38.125 |
| and 50 hydrogen | . . | 1.059 |
| 100 cubic inches of muriatic acid gas must weigh | | 39.184 |

Its specific gravity, therefore, is 1.2847. By weight it consists of

| | | |
|---|---|---|
| Chlorine . | 38.125 . | 36 |
| Hydrogen . | 1.059 . | 1 |

Since chlorine and hydrogen unite in one proportion only, most chemists regard muriatic acid as a compound of one equivalent of each of its elements, a conclusion which appears to be justified by the proportions in which chlorine and hydrogen unite with other bodies. Hence, 36 is one equivalent of chlorine, and 37 the equivalent of muriatic acid.

Muriatic acid is a colourless gas, of a pungent odour, and acid taste. Under a pressure of 40 atmospheres, and at the temperature of 50° F. it is liquid. It is quite irrespirable, exciting violent spasm of the glottis; but when diluted with air, it is far less irritating than chlorine. All burning bodies are extinguished by it, and the gas itself does not take fire on the approach of flame.

Muriatic acid gas is not chemically changed by mere heat. It is readily decomposed by galvanism, hydrogen appearing at the negative, and chlorine at the positive pole. It is also decomposed by ordinary electricity. The decomposition, however, is incomplete; for though one electric spark resolves a portion of the gas into its elements, the next shock in a great measure effects their reunion. It is not affected by oxygen under common circumstances; but if a mixture of oxygen and muriatic acid gases is electrified, the oxygen unites with the hydrogen of the muriatic acid to form water, and chlorine is set at liberty. For this and the preceding fact we are indebted to the researches of Dr Henry.

## *Compounds of Chlorine and Oxygen.*

Chlorine unites with oxygen in four different proportions. The leading character of these compounds is derived from the circumstance that chlorine and oxygen, the attraction of which for most elementary substances is so energetic, have but a feeble affinity for one another. These principles, consequently, are never met with in nature in a state of combination. Indeed, they cannot be made to combine directly; and when they do unite, very slight causes effect their separation. Notwithstanding this, their union is always regulated by the law of definite proportions, as appears from the following tabular view of the constitution of the compounds to which they give rise*.

| | *Chlorine.* | *Oxygen.* |
|---|---|---|
| Protoxide of chlorine | 36 | 8 |
| Peroxide of chlorine | 36 | 32 |
| Chloric acid | 36 | 40 |
| Perchloric acid | 36 | 56 |

*Protoxide of Chlorine.*—This gas was discovered in 1811 by Sir H. Davy, and was described by him in the Philosophical Transactions for that year under the name of *Euchlorine*. It is made by the action of muriatic acid on chlorate of potassa; and its production is explicable by the fact, that muriatic and chloric acids mutually decompose each other. When muriatic acid and chlorate of potassa are mixed together, part of the muriatic acid unites with the potassa of the salt, and thus sets chloric acid free, which instantly reacts on the free muriatic acid. The result of the reaction depends on the relative quantity of the substances. If chlorate of potassa is mixed with an excess of concentrated muriatic acid, the chloric acid undergoes complete decomposition. For each equivalent of chloric, five equivalents of muriatic acid are decomposed: the five equivalents of oxygen contained in the former unite with the hydrogen of the latter, producing five equivalents of water; while the chlorine of both acids is disengaged. If, on the contrary, the chlorate of potassa is in excess, and the muriatic acid diluted, the chloric acid is deprived of part of its oxygen only; and the products are water, protoxide of chlorine, and chlorine, the two latter escaping in the gaseous form. From the relative proportion in which these gases are evolved, I apprehend that for each equivalent of chloric, three of muriatic acid must be decomposed; and that by the reaction of their elements, they yield three equivalents of water, two of pure chlorine, and two of the protoxide of chlorine.

The best proportion of the ingredients for forming this compound is two parts of chlorate of potassa, one of strong muriatic acid, and one of water; and the reaction of the materials should be promoted by heat sufficient to produce moderate effervescence. The gases should be collected over mercury, which combines with the chlorine, and leaves the protoxide of chlorine in a pure state.

The protoxide of chlorine has a yellowish-green colour similar to that of chlorine, but considerably more brilliant, which induced Sir H. Davy to give it the name of *euchlorine*. Its odour is like that of burned sugar. Water dissolves eight or ten times its volume of the gas, and acquires a colour approaching to orange. It bleaches vegetable substances, but gives the blue colours a tint of red before de-

* Note by Gay-Lussac in the 9th volume of the An. de Ch. et de Physique.

stroying them. It does not unite with alkalies, and therefore is not an acid.

The protoxide of chlorine is explosive in a high degree. The heat of the hand, or the pressure occasioned in transferring it from one vessel to another, sometimes causes an explosion. This effect is also occasioned by phosphorus, which bursts into flame at the moment of immersion. All burning bodies, by their heat, occasion an explosion, and then burn vividly in the decomposed gas. With hydrogen it forms a mixture which explodes by flame or the electric spark, with production of water and muriatic acid. The best proportion is fifty measures of the protoxide of chlorine to eighty of hydrogen.

The protoxide of chlorine is easily analyzed by heating a known quantity of it in a strong tube over mercury. An explosion takes place; and 50 of the gas expand to 60 measures, 20 of which are oxygen, and 40 chlorine. The specific gravity of a gas so constituted must be 2.444, and its composition by weight is, chlorine 36 + oxygen 8. Its atomic weight is consequently 44.

*Peroxide of Chlorine.*—The peroxide of chlorine was discovered in 1815 by Sir H. Davy*, and soon after by Count Stadion of Vienna. It is formed by the action of sulphuric acid on chlorate of potassa. A quantity of this salt, not exceeding 50 or 60 grains, is reduced to powder, and made into a paste by the addition of strong sulphuric acid. The mixture, which acquires a deep yellow colour, is placed in a glass retort, and heated by warm water, the temperature of which is kept under 212° F. A bright yellowish-green gas of a still richer colour than the protoxide of chorine is disengaged, which has an aromatic odour without any smell of chlorine, is absorbed rapidly by water, to which it communicates its tint, and has no sensible action on mercury. This gas is the peroxide of chlorine.

The chemical changes which take place in the process are explained in the following manner. The sulphuric acid decomposes some of the chlorate of potassa, and sets chloric acid at liberty. The chloric acid, at the moment of separation, resolves itself into peroxide of chlorine and oxygen; the last of which, instead of escaping as free oxygen gas, goes over to the acid of some undecomposed chlorate of potassa, and converts it into perchloric acid. The whole products are bisulphate and perchlorate of potassa, and peroxide of chlorine. It is most probable, from the data contained in the preceding table, that every three equivalents of chloric acid yield one equivalent of perchloric acid and two equivalents of peroxide of chlorine.

The peroxide of chlorine does not unite with alkalies. It destroys most vegetable blue colours without previously reddening them. Phosphorus takes fire when introduced into it, and occasions an explosion. It explodes violently when heated to a temperature of 212° F, emits a strong light, and undergoes a greater expansion than the protoxide of chlorine. According to Sir H. Davy, whose result is confirmed by Gay-Lussac, 40 measures of the gas occupy the space of 60 measures after explosion; and of these, 20 are chlorine and 40 oxygen. The peroxide is therefore composed of 36 parts or one equivalent of chlorine, united with 32 or four equivalents of oxygen. Its specific gravity must be 2.361.

*Chloric acid.*—When to a dilute solution of the chlorate of baryta a quantity of weak sulphuric acid, exactly sufficient for combining with the baryta, is added, the insoluble sulphate of baryta subsides,

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* Philosophical Transactions for 1815.

and pure chloric acid remains in the liquid. This acid, the existence of which was originally observed by Mr Chenevix, was first obtained in a separate state by Gay-Lussac.

Chloric acid reddens vegetable blue colours, has a sour taste, and forms neutral salts, called *chlorates*, (formerly *hyperoxymuriates*) with alkaline bases. It possesses no bleaching properties, a circumstance by which it is distinguished from chlorine. It gives no precipitate in solution of nitrate of silver, and hence cannot be mistaken for muriatic acid. Its solution may be concentrated by gentle heat, till it acquires an oily consistence, without decomposition; but at a higher temperature, the acid in part is volatilized unchanged, while another portion is converted into chlorine and oxygen. It is easily decomposed by deoxidizing agents. Sulphurous acid, for instance, deprives it of oxygen, with formation of sulphuric acid and evolution of chlorine. By the action of sulphuretted hydrogen, water is generated, while sulphur and chlorine are set free. The power of muriatic acid in effecting its decomposition has already been explained.

Chloric acid is readily known by forming a salt with potassa, which crystallizes in tables and has a pearly lustre, which deflagrates like nitre when flung on burning charcoal, and yields peroxide of chlorine by the action of concentrated sulphuric acid. Chlorate of potassa, like most of the chlorates, gives off pure oxygen when heated to redness, and leaves a residue of the chloride of potassium. This was the mode by which Gay-Lussac ascertained the composition of chloric acid, as stated in the table. (Annales de Chimie, vol. xci.)

*Perchloric acid.*—The saline matter which remains in the retort after forming the peroxide of chlorine, is a mixture of perchlorate and bisulphate of potassa; and by washing it with cold water, the bisulphate is dissolved, and the perchlorate is left. Perchloric acid may be prepared from this salt by mixing it in a retort with half its weight of sulphuric acid, diluted with one-third of water, and applying heat to the mixture. At the temperature of about 284° F. white vapours rise, which condense as a colourless liquid in the receiver. This is a solution of perchloric acid.

The properties of perchloric acid have hitherto been little examined. Count Stadion*, its discoverer, found it to be a compound of one equivalent or 36 parts of chlorine, to 56 or seven equivalents of oxygen; and his analysis has been confirmed by Gay-Lussac†.

## *Chloride of Nitrogen.*

The mutual affinity of chlorine and nitrogen is very slight: they do not combine at all if presented to each other in their gaseous form; and when combined, they are easily separated. The chloride of nitrogen is formed by the action of chlorine on some salt of ammonia. Its formation is owing to the decomposition of ammonia (a compound of hydrogen and nitrogen) by chlorine. The hydrogen of the ammonia unites with chlorine, and forms muriatic acid; while the nitrogen of the ammonia, being presented in its nascent state to chlorine, dissolved in the solution, enters into combination with it.

A convenient method of preparing chloride of nitrogen is the following. An ounce of muriate of ammonia is dissolved in twelve or sixteen ounces of hot water; and when the solution has cooled to the temperature of 90° F. a glass bottle, with a wide mouth, full of chlorine,

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* Annales de Ch. et de Physique, vol. viii. † Ibid. vol ix.

is inverted in it. The solution gradually absorbs the chlorine, and acquires a yellow colour; and in about twenty minutes or half an hour, minute globules of a yellow fluid are seen floating like oil upon its surface, which, after acquiring the size of a small pea, sink to the bottom of the liquid. The drops of chloride of nitrogen, as they descend, should be collected in a small saucer of lead, placed for that purpose under the mouth of the bottle.

The chloride of nitrogen, discovered in 1811 by M. Dulong, (An. de Chimie, vol. lxxxvi.) is one of the most explosive compounds yet known, having been the cause of serious accidents both to its discoverer and to Sir H. Davy*. Its specific gravity is 1.653. It does not congeal by the intense cold produced by a mixture of snow and salt. It may be distilled at 160° F., but at a temperature between 200° and 212° it explodes. It appears from the investigation of Messrs Porrett, Wilson, and Kirk†, that mere contact with some substances of a combustible nature cause detonation even at common temperatures. This property belongs particularly to the oils, both volatile and fixed. I have never known olive oil fail in producing the effect. The products of the explosion are chlorine and nitrogen.

Sir H. Davy analyzed the chloride of nitrogen by means of mercury, which unites with chlorine, and liberates the nitrogen. He inferred from his analysis that its elements are united in the proportion of four measures of chlorine to one of nitrogen; and it hence follows that, by weight, it consists of

| | | |
|---|---|---|
| Chlorine . | 144 . | or four proportions. |
| Nitrogen . | 14 . | or one proportion‡. |

## *Compounds of Chlorine and Carbon.—Perchloride of Carbon.*

For the knowledge of the compounds of chlorine and carbon, chemists are indebted to the ingenuity of Mr Faraday. When olefiant gas (a compound of carbon and hydrogen) is mixed with chlorine, combination takes place between them, and an oily-like liquid is generated, which consists of chlorine, carbon, and hydrogen. On exposing this liquid in a vessel full of chlorine gas to the direct solar rays, the chlorine acts upon and decomposes the liquid, muriatic acid is set free, and the carbon, at the moment of separation, unites with chlorine§.

The *perchloride of carbon*, as this compound is named by Mr Faraday, is solid at common temperatures, has an aromatic odour approaching to that of camphor, is a non-conductor of electricity, and refracts light very powerfully. Its specific gravity is exactly double that of water. It fuses at 320° F. and after fusion it is colourless and very transparent. It boils at 360°, and may be distilled without

* Philosophical Transactions, 1813.

† Nicholson's Journal, vol. xxxiv.

‡ Berzelius states the composition of this compound to be three volumes of chlorine to one of nitrogen, corresponding to three equivalents of the former to one of the latter. These proportions, if found to be correct, will render the chloride and iodide of nitrogen, analogous in composition. B.

§ The reader will find the details of this process in the Philosophical Transactions for 1821, or in the second volume, N.S. of the Annals of Philosophy.

change, assuming a crystalline arrangement as it condenses. It is sparingly soluble in water, but dissolves in alcohol and ether, especially by the aid of heat. It is soluble also in fixed and volatile oils.

The perchloride of carbon burns with a red light when held in the flame of a spirit-lamp, giving out acid vapours and smoke; but the combustion ceases as soon as it is withdrawn. It burns vividly in oxygen gas. Alkalies do not act upon it; nor is it changed by the stronger acids, such as the muriatic, nitric, or sulphuric acids, even with the aid of heat. When its vapour is mixed with hydrogen, and passed through a red-hot tube, charcoal is separated, and muriatic acid gas evolved*. On passing its vapour over the peroxides of metals, such as those of mercury and copper, heated to redness, a chloride of the metal and carbonic acid are generated. Protoxides, under the same treatment, yield carbonic oxide gas and a metallic chloride. Most of the metals decompose it also at the temperature of ignition, uniting with the chlorine, and causing deposition of charcoal.

From the proportions of chlorine and olefiant gas employed in forming the perchloride of carbon, and from its analysis, made by passing it over peroxide of copper at the temperature of ignition, Mr Faraday infers that this compound consists of

| | | | | |
|---|---|---|---|---|
| Chlorine | . | 108 | . | or three proportionals. |
| Carbon | . | 12 | . | or two proportionals. |

*Protochloride of carbon.*—When the vapour of the perchloride of carbon is passed through a red-hot glass or porcelain tube, containing fragments of rock crystal to increase the extent of heated surface, partial decomposition takes place; chlorine gas escapes, and a fluid passes over which Mr Faraday calls the *protochloride of carbon*.

The protochloride of carbon is a limpid colourless fluid, which does not congeal at zero of Fahrenheit, and at 160° or 170° F. is converted into vapour. It may be distilled repeatedly without change; but when exposed to a red heat, some of it is resolved into its elements. Its specific gravity is 1.5526. In its chemical relations it is very analogous to the perchloride of carbon. Mr Faraday analyzed it by transmitting its vapour over ignited peroxide of copper, and infers from the products of its decomposition—carbonic acid and chloride of copper—that it is composed of

| | | | | |
|---|---|---|---|---|
| Chlorine | . | 36 | . | or one proportional. |
| Carbon | . | 6 | . | or one proportional. |

A third compound of chlorine and carbon is described in the first volume, New Series, of the Annals of Philosophy. It was brought from Sweden by M. Julin, and is said to have been formed during the distillation of nitric acid from crude nitre, and sulphate of iron. It occurs in small, soft, adhesive fibres of a white colour, which have a peculiar odour, somewhat resembling spermaceti. It fuses on the application of heat, and boils at a temperature between 350° and 450°

* As the text originally stood, it read as follows:—"Alkalies do not act upon it; nor is it changed by the stronger acids, such as the muriatic, nitric, or sulphuric acids, even with the aid of heat; charcoal is separated, and muriatic acid gas evolved." There is evidently some omission here, as the last clause of the sentence does not make sense with what precedes it. The words which have been supplied are evidently necessary to complete the sense; but before I felt satisfied to insert them, I consulted the original paper of Mr Faraday in the Philosophical Transactions, and find that it clearly justifies the addition which I have made. B.

F. At 250° F. it sublimes slowly, and condenses again in the form of long needles. It is insoluble in water, acids, and alkalies; but is dissolved by hot oil of turpentine or by alcohol, and forms acicular crystals as the solution cools. It burns with a red flame, emitting much smoke, and fumes of muriatic acid gas.

The nature of this substance is shown by the following circumstances. When its vapour is exposed to a red heat, evolution of chlorine gas ensues, and charcoal is deposited. A similar deposition of charcoal is produced by heating it with phosphorus, iron, or tin, and a chloride is formed at the same time. Potassium burns vividly in its vapour, with formation of chloride of potassium, and separation of charcoal. On detonating a mixture of its vapour with oxygen gas over mercury, a chloride of that metal and carbonic acid are generated. From these facts, the greater part of which were ascertained by Messrs Phillips and Faraday*, it follows that the substance brought from Sweden by M. Julin is a compound of chlorine and carbon; and the same able chemists conclude from their analysis that its elements are united in the proportion of

| | | |
|---|---|---|
| Chlorine | . | 36, or one equivalent. |
| Carbon | . | 12, or two equivalents. |

## *Chloride of Sulphur.*

The *Chloride of Sulphur* was discovered in the year 1804 by Dr Thomson†, and was afterwards examined by Berthollet‡. It is most conveniently prepared by passing a current of chlorine gas over flowers of sulphur gently heated. Direct combination takes place, and the product is obtained under the form of a liquid which appears red by reflected, and yellowish-green by transmitted light. Its density is 1.6. It is volatile below 200° F. and condenses again without change in cooling. When exposed to the air it emits acrid fumes, which irritate the eyes powerfully, and have an odour somewhat resembling sea-weed, but much stronger. Dry litmus paper is not reddened by it, nor does it unite with alkalies. It acts with energy on water;—mutual decomposition ensues, the water becomes cloudy from deposition of sulphur, and a solution is obtained, in which muriatic, sulphurous, and sulphuric acids, may be detected. Similar phenomena ensue when it is mixed with alcohol or ether.

Sir H. Davy concludes from his experiments, (Elements, p. 280,) that the chloride of sulphur is composed of 30 parts of sulphur, and 68.4 of chlorine. This proportion leaves little doubt of its being a compound of 36 or one equivalent of chlorine, and 16 or one equivalent of sulphur.

## *Compounds of Chlorine and Phosphorus.*

There are two definite compounds of chlorine and phosphorus, the nature of which was first satisfactorily explained by Sir H. Davy, (Elements, p. 290.) When phosphorus is introduced into a jar of dry chlorine, it inflames, and a white matter collects on the inside of the vessel, which is the *perchloride of phosphorus*. It is very volatile, a temperature much below 212° F. being sufficient to convert it into

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* Annals of Philosophy, second vol. N. S. p. 150.
† Nicholson's Journal, vol. vi.
‡ Memoires d'Arcueil, vol. i.

vapour. Under pressure it may be fused, and yields transparent prismatic crystals in cooling.

Water and perchloride of phosphorus mutually decompose each other; and the sole products are muriatic and phosphoric acids. Now in order that these products should be formed, consistently with the constitution of phosphoric acid, as stated at page 188, the perchloride must consist of 15.71 parts or one equivalent of phosphorus, and 90 parts or two equivalents and a half of chlorine. One equivalent of the choride and two and a half of water, will then mutually decompose each other without any element being in excess, and yield one equivalent of phosphoric and two and a half equivalents of muriatic acid. This proportion is not far from the truth; for Sir H. Davy states, that in the perchloride one grain of phosphorus is united with six of chlorine.

The *protochloride of phosphorus* may be made either by heating the perchloride with phosphorus, or by passing the vapour of phosphorus over corrosive sublimate contained in a glass tube. It is a clear liquid like water, of specific gravity 1.45; emits acid fumes when exposed to the air, owing to the decomposition of watery vapour; but when pure it does not redden dry litmus paper. On mixing it with water, mutual decomposition ensues, heat is evolved, and a solution of muriatic and phosphorous acids is obtained. It hence appears to consist of 15.71 parts, or one proportional of phosphorus, and 54 parts, or one proportional and a half of chlorine.

## *Chlorocarbonic Acid Gas.*

This compound was discovered in 1812 by Dr John Davy, who described it in the Philosophical Transactions for that year, under the name of *phosgene gas**. It is made by exposing a mixture of equal measures of dry chlorine and carbonic oxide gases to sunshine, when rapid but silent combination ensues, and they contract to one-half their volume. Diffused day-light also effects their union slowly; but they do not combine at all when the mixture is wholly excluded from light.

*Chlorocarbonic acid gas* is colourless, has a strong odour, and reddens dry litmus paper. It combines with four times its volume of ammoniacal gas, forming a white solid salt; so that it possesses the characteristic property of acids. It is decomposed by contact with water. One equivalent of each compound undergoes decomposition; and as the hydrogen of the water unites with cholorine, and its oxygen with carbonic oxide, the products are carbonic and muriatic acids. When tin is heated in chlorocarbonic acid gas, the chloride of tin is generated, and carbonic oxide gas set free, which occupies exactly the same space as the chlorocarbonic acid which was employed. A similar change occurs when it is heated in contact with antimony, zinc, or arsenic.

As chlorocarbonic acid gas contains its own volume of both its constituents, it follows that 100 cubic inches of that gas, at the standard temperature and pressure must weigh 105.9 grains; namely, 76.25 of chlorine added to 29.65 of carbonic oxide. Its specific gravity is therefore 3.4721; and it consists of

| | | |
|---|---|---|
| Chlorine | 36 | or one proportion. |
| Carbonic oxide | 14 | or one proportion. |

* From φως light and γενναω I produce.

## Chloride of Boron.

Sir H. Davy noticed that recently prepared boron takes fire spontaneously in an atmosphere of chlorine, and emits a vivid light; but he did not examine the product. Berzelius remarked, that if the boron has been previously heated, whereby it is rendered more compact, the combustion does not take place till heat is applied. This observation led him to expose boron, thus rendered dense, in a glass tube to a current of dry chlorine, and to heat it gently, so as to commence the combustion as soon as the atmospheric air was completely expelled. The resulting compound proved to be a colourless gas, and, on collecting it over mercury, which absorbed free chlorine, he procured the chloride of boron in a state of purity. This gas is rapidly absorbed by water, and double decomposition takes place at the same instant, giving rise to the production of muriatic and boracic acids. The watery vapour of the atmosphere occasions a similar change, so that when the gas is mixed with air containing hygrometric moisture, a dense white cloud is produced. The specific gravity of the gas, according to Dumas, is 3.942. It is soluble in alcohol, and communicates to it an ethereal odour, apparently by the action of muriatic acid. It unites with ammoniacal gas, forming a fluid volatile substance, the nature of which is unknown.—(Annals of Phil. xxvi. 129.)

M. Dumas finds, that chloride of boron may be generated by the action of dry chlorine on a mixture of charcoal and boracic acid, heated to redness in a porcelain tube. M. Despretz also appears to have invented a similar process.—(Philos. Magazine and Annals, i. 469)

The composition of the chloride of boron may be inferred from its action on water. If the constitution of boracic acid, as ascertained by Dr Thomson, is correct, (page 191) the chloride of boron should consist of 72 parts or two equivalents of chlorine, and 8 parts or one equivalent of boron; for one equivalent of such a compound, with two of water, will yield one of boracic and two equivalents of muriatic acid.

## On the Nature of Chlorine.

The change of opinion which has gradually taken place among chemists concerning the nature of chlorine, is a remarkable fact in the history of the science. The hypothesis of Berthollet, unfounded as it is, prevailed at one time universally. It explained phenomena so satisfactorily, and in a manner so consistent with the received chemical doctrine, that for some years no one thought of calling its correctness into question. A singular reverse, however, has taken place. Though this view has not hitherto been rigidly demonstrated to be erroneous, it has within a short period been generally abandoned, even by persons who, from having adopted it in early life, were prejudiced in its favour. The reason of this will readily appear on comparing the two theories, and examining the evidence in favour of each.

Chlorine, according to the new theory, is maintained to be a simple body, because, like oxygen, hydrogen, and other analogous substances, it cannot be resolved into more simple parts. It does not indeed follow that a body is simple, because it has not hitherto been decomposed; but as chemists have no other mode of estimating the elementary nature of bodies, they must necessarily adopt this one, or have none at all. Muriatic acid, by the same rule, is considered to be a compound of chlorine and hydrogen. For when it is exposed to

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the agency of galvanism, it is resolved into these substances; and by mixing the two gases in due proportion, and passing an electric spark through the mixture, muriatic acid gas is the product. Chemists have no other kind of proof of the composition of water, of potassa, or of any other compound.

Very different is the evidence in support of the theory of Berthollet. Acccording to that view, muriatic acid gas is composed of *absolute muriatic acid*, and water or its elements; chlorine consists of *absolute muriatic acid* and oxygen; and *absolute muriatic acid* is a compound of a certain unknown base and oxygen gas. Now all these propositions are gratuitous. For, in the first place, muriatic acid gas has not been proved to contain water. Secondly, the assertion that chlorine contains oxygen is opposed to direct experiment, the most powerful deoxidizing agents having been unable to deprive that gas of a particle of oxygen. Thirdly, the existence of such a substance as *absolute muriatic acid* is wholly without proof, and therefore its supposed base is also imaginary.

But this is not the only weak point of the doctrine. Since chlorine is admitted by this theory to contain oxygen, it was necessary to explain how it happens that no oxygen can be separated from it. Thus, on exposing chlorine to a powerful galvanic battery, oxygen gas does not appear at the positive pole, as occurs when other oxidized bodies are subjected to its action; nor is carbonic acid or carbonic oxide evolved, when chlorine is conducted over ignited charcoal. To account for the oxygen not appearing under these circumstances, it was assumed that *absolute muriatic acid* is unable to exist in an uncombined state, and therefore cannot be separated from one substance except by uniting with another. This supposition was thought to be supported by the analogy of certain compounds, such as nitric and oxalic acids, which appear to be incapable of existing except when combined with water or some other substance. The analogy, however, is incomplete; for the decomposition of such compounds, when an attempt is made to procure them in an insulated state, is manifestly owing to the tendency of their elements to enter into new combinations.

Admitting the various assumptions which have been stated, most of the phenomena receive as consistent an explanation by the old as by the new theory. Thus, when muriatic acid gas is resolved by galvanism into chlorine and hydrogen, it may be supposed that the *absolute muriatic acid* attaches itself to the oxygen of the water, and forms chlorine, while the hydrogen of the water is attracted to the opposite pole of the battery. When chlorine and hydrogen enter into combination, the oxygen of the former may be said to unite with the latter, and that muriatic acid gas is generated by the water so formed combining with the *absolute muriatic acid* of the chlorine. The evolution of chlorine, which ensues on mixing muriatic acid and peroxide of manganese, is explained on the supposition that *absolute muriatic acid* unites directly with the oxygen of the black oxide of manganese.

It will not be difficult after these observations to account for the preference shown to the new theory. In an exact science, such as chemistry, every step of which is required to be matter of demonstration, there is no room to hesitate between two modes of reasoning, one of which is hypothetical, and the other founded on experiment. Nor is there, in the present instance, temptation to deviate from the strict logic of the science; for there is not a single phenomenon which may not be fully explained on the new theory, in a manner quite consistent with the laws of chemical action in general. It was supposed,

indeed, at one time, that the sudden decomposition of water, occasioned by the action of that liquid on the compounds of chlorine with some simple substances, constitutes a real objection to the doctrine; but it will afterwards appear, that the acquisition of new facts has deprived this argument of all its force. While nothing therefore can be gained, much may be lost by adopting the doctrine of Berthollet. If chlorine is regarded as a compound body, the same opinion, though in direct opposition to the result of observation, ought to be extended to iodine and bromine; and as other analogous substances may hereafter be discovered, in regard to which a similar hypothesis will apply, it is obvious that this view, if proper in one case, may legitimately be extended to others. One encroachment on the method of strict induction would consequently open the way to another, and thus the genius of the science would eventually be destroyed.

An able attempt was made some years ago by the late Dr Murray, to demonstrate the presence of water or its elements as a constituent part of muriatic acid gas, and thus to establish the old theory to the subversion of the new. Into this discussion, however, I shall not enter here, as it would lead into details too minute for an elementary treatise. I may only observe, in referring the reader to the original papers on the subject*, that Dr Murray did not succeed in establishing his point; and that his arguments, though exceedingly plausible and ingenious, were fully answered by Sir Humphry and Dr John Davy. I must also state, that the history of the only experiment which strictly bears upon the question,—that, namely, in which muriatic acid and ammoniacal gases were mixed together, amounts very nearly to a demonstration of the absence of combined water in muriatic acid gas. The traces of humidity, which were observed, may easily be accounted for by the difficulty of rendering gases absolutely dry, which have themselves a strong affinity for moisture; whereas the absence of so large a quantity of water, as ought, according to Dr Murray's argument, to be present in muriatic acid gas, does not admit of a satisfactory explanation, except by supposing that gas to be anhydrous.

## SECTION XII.

### *IODINE.*

Iodine was discovered in the year 1812 by M. Courtois, a manufacturer of saltpetre at Paris. In preparing carbonate of soda from the ashes of sea-weeds, he observed that the residual liquor corroded metallic vessels powerfully; and in investigating the cause of the corrosion, he noticed that sulphuric acid threw down a dark coloured matter, which was converted by the application of heat into a beautiful violet vapour. Struck with its appearance, he gave some of the substance to M. Clement, who recognised it as a new body, and in 1813 described some of its leading properties in the Royal Institute of France. Its real nature was soon after determined by Gay-Lussac and

* In Nicholson's Journal, vols. xxxi. xxxii. and xxxiv. Edinburgh Philos. Trans. vol. viii. and Philos. Trans. for 1818.

Sir H. Davy, each of whom proved that it is a simple non-metallic substance, exceedingly analogous to chlorine*.

Iodine, at common temperatures, is a soft friable opake solid, of a bluish-black colour, and metallic lustre. It occurs usually in crystalline scales, having the appearance of micaceous iron-ore; but it sometimes crystallizes in large rhomboidal plates, the primitive form of which is an octahedron. Its specific gravity, according to Gay-Lussac, is 4.948; but Dr Thomson found it only 3.0844. At 225° F. it is fused, and enters into ebullition at 347°; but when moisture is present, it is sublimed rapidly even below the degree of boiling water, and suffers a gradual dissipation at low temperatures. Its vapour is of an exceedingly rich violet colour, a character to which it owes the name of *Iodine*†. This vapour is remarkably dense, its specific gravity, as calculated by the formula of page 129, being 8.6102; or 8.716 as directly observed by M. Dumas. Hence 100 cubic inches, at the standard temperature and pressure, must weigh 262.612 grains. Dr Thomson infers, partly from the experiments of Gay-Lussac, and partly from his own researches, that the atomic weight of iodine is 124.

Iodine is a non-conductor of electricity, and, like oxygen and chlorine, is a negative electric. It has a very acrid taste, and its odour is almost exactly similar to that of chlorine, when much diluted with air. It acts energetically on the animal system as an irritant poison, but is employed with advantage in medicine in very small doses.

Iodine is very sparingly soluble in water, requiring about 7000 times its weight of that liquid for solution. It communicates, however, even in this minute quantity, a brown tint to the menstruum. Alcohol and ether dissolve it freely, and the solution has a deep reddish-brown colour.

Iodine possesses an extensive range of affinity. It destroys vegetable colours, though in a much less degree than chlorine. It manifests little disposition to combine with metallic oxides; but it has a strong attraction for the pure metals, and for most of the simple non-metallic substances, producing compounds which are termed *Iodides* or *Iodurets*. It is not inflammable; but under favourable circumstances may, like chlorine, be made to unite with oxygen. A solution of the pure alkalies acts upon it in the same manner as upon chlorine, giving rise to the decomposition of water and the formation of iodic and hydriodic acids.

Pure iodine is not influenced chemically by the imponderables. Exposure to the direct solar rays, or to strong shocks of electricity, does not change its nature. It may be passed through red-hot tubes, or over intensely ignited charcoal, without any appearance of decomposition; nor is it affected by the agency of galvanism. Chemists, indeed, are unable to resolve it into more simple parts, and consequently it is regarded as an elementary principle.

The violet hue of the vapour of iodine is for many purposes a sufficiently sure indication of its presence. A far more delicate test, however, was discovered by MM. Colin and Gaultier de Claubry. They found that iodine has the property of uniting with starch, and of forming with it a compound insoluble in cold water, which is recognised with certainty by its deep blue colour. This test, according to Professor

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* The original papers on this subject are in the Annales de Chimie, vols. lxxxviii. xc. and xci.; and in the Philos. Trans. for 1814 and 1815.

† From Ἰώδης *violaceus*.

Stromeyer, is so delicate, that a liquid containing 1—450,000 of its weight of iodine, receives a blue tinge from a solution of starch. Two precautions should be observed to insure success. In the first place, the iodine must be in a free state; for it is the iodine itself only, and not its compounds, which unite with starch. Secondly, the solution should be quite cold at the time of adding the starch; for boiling water decomposes the blue compound, and consequently removes its colour.

## *Iodine and Hydrogen—Hydriodic Acid Gas.*

When a mixture of hydrogen and the vapour of iodine is transmitted through a red-hot porcelain tube, direct combination takes place between them, and a colourless gas, possessed of acid properties, is the product. To this substance the term *Hydriodic acid gas* is applied.

This gas may be obtained quite pure by the action of water on iodide of phosphorus. Any convenient quantity of moistened iodine is put into a small glass retort, and about one-twelfth of its weight of phosphorus is then added. An iodide of phosphorus is formed, which instantly reacts upon water. Mutual decomposition ensues; the oxygen of the water unites with phosphorus, and its hydrogen with iodine, giving rise to the formation of phosphoric and hydriodic acids. On the application of a moderate heat, the latter passes over in the form of a colourless gas.

The hydriodic acid gas has a very sour taste, reddens vegetable blue colours without destroying them, produces dense white fumes when mixed with atmospheric air, and has an odour similar to that of muriatic acid gas. It combines with alkalies, forming salts which are called *hydriodates*. Like muriatic acid gas it cannot be collected over water; for that liquid dissolves it in large quantity.

Hydriodic acid is decomposed by several substances which have a strong affinity for either of its elements. Thus oxygen gas, when heated with it, unites with the hydrogen, and liberates the iodine. Chlorine effects the decomposition instantly; muriatic acid gas is produced, and the iodine appears in the form of vapour. With the strong nitrous acid of the Edinburgh Pharmacopœia it takes fire, and the vapour of iodine is set free. It is also decomposed by mercury. The decomposition begins as soon as hydriodic acid comes in contact with mercury, and proceeds steadily, and even quickly if the gas is agitated, till nothing but hydrogen remains. Gay-Lussac ascertained by this method that 100 measures of hydriodic acid gas contain precisely half their volume of hydrogen. This result induced him to suspect that the composition of hydriodic must be analogous to that of muriatic acid gas; that, as 100 measures of the latter contain 50 of hydrogen and 50 of chlorine, 100 measures of the former consist of 50 of hydrogen and 50 of the vapour of iodine. If this view be correct, then the composition of hydriodic acid gas, by weight, may be determined by calculation. For since

| | | Grains. |
|---|---|---|
| 50 | cubic inches of the vapour of iodine weigh | 131.306 |
| 50 | . . hydrogen gas . . | 1.059 |
| 100 | cubic inches of hydriodic acid gas must weigh | 132.365 |

and its specific gravity will be 4.3398. Now Gay-Lussac ascertained, by weighing the hydriodic acid gas, that its density is 4.443,—a number which corresponds so closely with the preceding, as to leave no

doubt that the principle of the calculation is correct. There is good reason to believe, indeed, that the calculated result, if not rigidly exact, is very near the truth; for Gay-Lussac states, that the number determined by him directly is too high. (Ann. de Chimie, vol. xci. p. 16.)

Since iodine and hydrogen unite in one proportion only, hydriodic acid is regarded as a compound of one equivalent of each element,—an opinion supported both by the proportions of which iodine combines with other substances, and by the analogy of muriatic acid. The constitution of hydriodic acid may therefore be thus stated:

| | *By Volume.* | *By Weight.* |
|---|---|---|
| Iodine | 50 | 124 or one proportional. |
| Hydrogen | 50 | 1 or one proportional. |
| | 100 | 125 |

and its combining proportion is 125.

When hydriodic acid gas is conducted into water till that liquid is fully charged with it, a colourless acid solution is obtained, which emits white fumes on exposure to the air, and has a density of 1.7. It may be prepared also by transmitting a current of sulphuretted hydrogen gas through water in which iodine in fine powder is suspended. The iodine, from having greater affinity than sulphur for hydrogen, decomposes the sulphuretted hydrogen; and hence sulphur is set free, and hydriodic acid produced. As soon as the iodine has disappeared, and become colourless, it is heated for a short time to expel the excess of sulpuretted hydrogen, and subsequently filtered to separate free sulphur.

The solution of hydriodic acid is readily decomposed. Thus, on exposure during a few hours to the atmosphere, the oxygen of the air forms water with the hydrogen of the acid, and sets iodine free. The solution is found to have acquired a yellow tint from the presence of uncombined iodine, and a blue colour is occasioned by the addition of starch. Nitric and sulphuric acids likewise decompose it by yielding oxygen, the former being at the same time converted into nitrous, and the latter into sulphurous acid. Chlorine unites directly with the hydrogen of the hydriodic acid, and muriatic acid is formed. The separation of iodine in all these cases may be proved in the way just mentioned. These circumstances afford a sure test of the presence of hydriodic acid, whether free or in combination with alkalies. All that is necessary, is to mix a cold solution of starch with the liquid, previously concentrated by evaporation if necessary, and then add a few drops of strong sulphuric acid. A blue colour will make its appearance if hydriodic acid is present.

Hydriodic acid is frequently met with in nature in combination with potassa or soda. Under this form it occurs in many salt and other mineral springs. It has been detected in the water of the Mediterranean, in the oyster, and some other marine molluscous animals, in sponges, and in most kinds of sea-weed. In some of these productions, such as the *Fucus serratus* and *Fucus digitatus*, it exists ready formed, and according to Dr Fyfe (Edinburgh Philos. Journal, I. 254) may be separated by the action of water; but in others it can be detected only after incineration. The marine animals and plants doubtless derive the hydriodic acid they contain from the sea. Vauquelin has found it also in the mineral kingdom, in combination with silver. (Annales de Chimie et de Physique, vol. xxix.)

All the iodine of commerce is procured from the impure carbonate

of soda, called kelp, which is prepared in large quantity on the northern shores of Scotland, by incinerating sea-weeds. The kelp is employed by soap-makers for the preparation of carbonate of soda; and the dark residual liquor, remaining after that salt has crystallized, contains a considerable quantity of hydriodic acid, combined with soda or potassa. By adding a sufficient quantity of sulphuric acid, the hydriodic acid is separated from the alkali, and then decomposed. The iodine sublimes when the solution is boiled, and may be collected in cool glass receivers. A more convenient process is to employ a moderate excess of sulphuric acid, and then add some of the peroxide of manganese to the mixture. The oxygen of the manganese decomposes the hydriodic acid, and protosulphate of manganese is formed. (Dr Ure's Paper in the 50th volume of the Philosophical Magazine.)

## *Iodine and Oxygen.—Iodic Acid.*

Iodic acid was discovered about the same time by Gay-Lussac and Sir H. Davy; but the latter first succeeded in obtaining it in a perfectly pure state. When iodine is brought into contact with protoxide of chlorine, immediate action ensues; the chlorine of the protoxide unites with one portion of iodine, and its oxygen with another, forming two compounds, a volatile orange-coloured matter, the chloriodic acid, and a white solid substance, which is *iodic acid*. On applying heat, the former passes off in vapour, and the latter remains. (Philos. Trans. for 1815.)

This compound, which was termed *oxiodine* by Sir H. Davy, is *anhydrous iodic acid*. It is a white semitransparent solid, which has a strong astringent sour taste, but no odour. Its density is considerable, as it sinks rapidly in sulphuric acid. When heated to the temperature of about 500° F. it is fused, and at the same time resolved into oxygen and iodine.

Iodic acid deliquesces in a moist atmosphere, and is very soluble in water. The liquid acid thus formed reddens vegetable blue colours, and afterwards destroys them. On evaporating the solution, a thick mass of the consistence of paste is left, which is hydrous iodic acid, and from which, by cautious application of heat, the water may be expelled. It acts powerfully on inflammable substances. With charcoal, sulphur, sugar and similar combustibles, it forms mixtures which detonate when heated. It enters into combination with metallic oxides, and the resulting salts are called *iodates*. These compounds, like the chlorates, yield pure oxygen by heat, and deflagrate when thrown on burning charcoal.

Iodic acid unites with several of the acids, such as the sulphuric, nitric, phosphoric, and boracic acids; and with the three first it forms crystallizable compounds. It is decomposed by sulphurous, phosphorous, and hydriodic acids, and by sulphuretted hydrogen. Iodine in each case is set at liberty, and may be detected as usual by starch. Muriatic and iodic acids decompose each other, water and chloriodic acid being generated.

Sir H. Davy analyzed iodic acid by determining the quantity of oxygen which it evolves when decomposed by heat. Gay-Lussac effected the same object by heating iodate of potassa, when pure oxygen was given off, and iodide of potassium remained. From the result of these analyses, it appears that iodic acid is a compound of 124 parts, or one equivalent of iodine, and 40 parts or five equivalents of oxygen. The sum of these numbers, or 164, is therefore the combining proportion of the acid.

*Iodous acid.* This name was applied to a compound prepared in 1824 by Professor Sementini of Naples by the action of iodine on chlorate of potassa. (Quarterly Journal of Science, XVII. 381.) Equal parts of the materials are triturated together in a glass or porcelain morter, until they form a very fine pulverulent yellow mass, in which the metallic lustre of the iodine is no longer perceptible. The mixture is then heated in a glass retort; and as soon as the chlorate begins to lose oxygen, iodous acid rises in the form of a dense white vapour, and condenses in the neck of the retort into a yellow liquid, which falls in drops into the receiver.

The liquid thus formed is of an oily consistence, and of a peculiarly disagreeable odour, somewhat resembling euchlorine. It has an acid astringent taste, and leaves a burning sensation on the tongue. It reddens vegetable blue colours permanently, without destroying them. With water and alcohol it forms amber-coloured solutions. Its density is greater than that of water. It is rapidly volatilized at 212° F, and evaporates slowly at common temperatures. It is decomposed by sulphur, and phosphorus and potassium take fire as soon as they come in contact with it.

After repeating the experiments of Sementini and examining the product, M. Wöhler asserts that it does not consist of iodine and oxygen, but chlorine and iodine. Part of the chloric acid, it appears is decomposed; but its elements, uniting with separate portions of iodine, yield iodic acid, which remains in the retort combined with potassa, and chloride of iodine, similar to that described by Gay-Lussac, which is sublimed. (Edin. Journ. of Science, No. XII. 352.) From some other experiments, however, M. Sementini has almost proved the existence both of iodous acid and an oxide of iodine. He states that on bringing together the vapour of iodine and oxygen gas considerably heated, the violet tint of the former disappears, and a yellow matter of the consistence of solid oil is generated. This he regards as the oxide of iodine; and if the supply of oxygen is kept up after its formation, it is converted into iodous acid similar to that above mentioned From the mode in which the process is described, there can scarcely be a doubt that some compound of iodine and oxygen is thus formed; but, at the same time, the new compounds have not been examined analytically, nor has the chemical constitution of the substances hitherto prepared by M. Sementini been determined with that accuracy required for inspiring confidence in his results. (Quarterly Journal of Science, N.S. I. 478.)

## *Chloriodic Acid.*

Chlorine is absorbed at common temperatures by dry iodine with evolution of caloric, and a solid compound of iodine and chlorine results, which was discovered both by Sir H. Davy and Gay-Lussac. The colour of the product is orange-yellow when the iodine is fully saturated with chlorine, but is of a reddish-orange if iodine is in excess. It is converted by heat into an orange-coloured liquid, which yields a vapour of the same tint on increase of temperature. It deliquesces in the open air, and dissolves freely in water. Its solution is colourless, is very sour to the taste, and reddens vegetable blue colours, but afterwards destroys them. From its acid properties Sir H. Davy gave it the name of *chloriodic acid*. Gay-Lussac, on the contrary, calls it *chloride of iodine*, conceiving that the acidity of its solution arises from the presence of muriatic and iodic acids, which he supposes to

be generated by the decomposition of water. The opinion of Sir H. Davy appears to me more probable; for we know that free muriatic and iodic acids mutually decompose each other, and therefore could hardly be generated by the action of water on the compound of iodine and chlorine. Chloriodic acid, however, does not unite with alkaline substances. On mixing it, for example, with baryta, the muriate and iodate of baryta are obtained. From this it may be inferred, that water and chloriodic acid react on each other when an alkali is present. The composition of chloriodic acid is not known with precision.

*Iodide of Nitrogen.*—From the weak affinity that exists between iodine and nitrogen, these substances cannot be made to unite directly. But when iodine is put into a solution of ammonia, the alkali is decomposed; its elements unite with different portions of iodine, and thus cause the formation of hydriodic acid and iodide of nitrogen. The latter subsides in the form of a dark powder, which is characterised, like chloride of nitrogen, by its explosive property. It detonates violently as soon as it is dried, and slight pressure, while moist, produces a similar effect. Heat and light are emitted during the explosion, and iodine and nitrogen are set free. According to the experiments of M. Colin, iodide of nitrogen consists of one proportional of nitrogen to three of iodine.

*Iodide of Phosphorus.*—Iodine and phosphorus combine readily in the cold, evolving so much caloric as to kindle the phosphorus, if the experiment is made in the open air; but in close vessels no light appears. The combination takes place in several proportions, which have not been determined. Its most interesting property is that of decomposing water, with formation of hydriodic and phosphoric acids.

*Iodide of Sulphur.*—This compound is formed by heating gently a mixture of iodine and sulphur. The product has a dark colour and radiated appearance, like antimony. Its elements are easily disunited by heat.

## SECTION XIII.

### *BROMINE.*

This peculiarly interesting substance was discovered about two years ago by M. Balard of Montpellier, and the first description of its properties appeared in the *Annales de Chimie et de Physique* for August 1826. The name originally applied to it was *muride;* but it has been since changed to *bromine*, a word derived from the Greek *βρωμος, graveolentia*, signifying a strong or rank odour. This appellation may be conveniently changed in English into that of *bromine.*

Bromine in its chemical relations bears a close analogy to chlorine and iodine, and has hitherto been always found in nature associated with the former, and sometimes also with the latter. It exists in sea water in the form of hydrobromic acid, combined, in the opinion of M. Balard, with magnesia. Its relative quantity, however, is very minute; and even the uncrystallizable residue called *bittern*, left after the muriate of soda has been separated from sea water by crystallization, contains it in small proportion. It may apparently be regarded as an essential ingredient of the saline matter of the ocean; for it has

been detected in the waters of the Mediterranean, Baltic, North Sea, and Frith of Forth. It has also been found in the waters of the Dead Sea, and in a variety of salt springs in Germany*. M. Balard found that it exists in marine plants growing on the shores of the Mediterranean, and he has procured it in appreciable quantity from the ashes of the sea-weeds that furnish iodine. He has likewise detected its presence in the ashes of some animals, especially in those of the *Janthina violacea*, one of the testaceous mollusca.

At common temperatures bromine is a liquid, the colour of which is blackish-red when viewed in mass and by reflected light, but appears hyacinth-red when a thin stratum is interposed between the light and the observer. Its odour, which somewhat resembles that of chlorine, is very disagreeable, and its taste powerful. Its specific gravity is about 3. Its volatility is considerable; for at common temperatures it emits red coloured vapours, which are very similar in appearance to those of nitrous acid; and at 116.5° F. it enters into ebullition. By a temperature between zero and —4° F. it is congealed, and in that state is brittle.

Bromine is a non-conductor of electricity, and undergoes no chemical change whatever from the agency of the imponderables. It may be transmitted through a red-hot glass tube, and be exposed to the agency of galvanism, without evincing the least trace of decomposition. Like oxygen, chlorine, and iodine, it is a negative electric. Bromine is soluble in water, alcohol, and ether, the latter being the best solvent. It does not redden litmus paper, but bleaches it rapidly like chlorine; and it likewise discharges the blue colour from a solution of indigo. Its vapour extinguishes a lighted taper; but before going out, it burns for a few seconds with a flame which is green at its base and red at its upper part. Some inflammable substances take fire by contact with bromine in the same manner as when introduced into an atmosphere of chlorine. It acts with energy on organic matters, such as wood or cork, and corrodes the animal texture; but if applied to the skin for a short time only, it communicates a yellow stain, which is less intense than that produced by iodine, and soon disappears. To animal life it is highly destructive, one drop of it placed on the beak of a bird having proved fatal.

From the close resemblance observable between chlorine and bromine, M. Balard was of course led to examine its relation with hydrogen, and found that these substances may readily be made to unite; the product of the combination being a gas very similar to muriatic and hydriodic acid gases, and which has hence received the name of *hydrobromic* acid gas. In its action on metals, also, bromine presents the closest similarity to that which chlorine exerts on the same substances. Antimony and tin take fire by contact with bromine; and its union with potassium is attended with such intense disengagement of heat as to cause a vivid flash of light, and often to burst the vessel in which the experiment is performed. Its affinity for metallic oxides is feeble, but it has a strong attraction for metals. By the action of alkalies it is resolved into hydrobromic and bromic acids, suffering the same kind of change as chlorine or iodine when similarly treated.

* Some of the salt springs of Germany furnish a good deal of bromine. The saline at Theodorshalle, near Kreuznach, contains a sufficient quantity to make its extraction profitable. A quintal (100 lbs.) of the mother-waters of this spring yields two ounces and one drachm of bromine.—*Berzelius*, *Traité de Chimie*, i. 293. B.

Bromine is usually extracted from bittern, and its mode of preparation is founded on the property which chlorine possesses of decomposing hydrobromic acid, uniting with its hydrogen, and setting bromine at liberty. Accordingly, on adding chlorine to bittern, the free bromine immediately communicates an orange-yellow tint to the liquid; and on heating the solution to the boiling point, the red vapours of bromine are expelled, and may be condensed by being conducted into a tube surrounded with ice. It was this change of colour produced by chlorine that led to the discovery of bromine. The method recommended by M. Balard for procuring this substance, as well as for detecting the presence of hydrobromic acid, is to transmit a current of chlorine gas through bittern, and then to agitate a portion of sulphuric ether with the liquid. The ether dissolves the whole of the bromine, from which it receives a beautiful hyacinth-red tint, and on standing rises to the surface. When the ethereal solution is agitated with caustic potassa, its colour entirely disappears, owing to the formation of hydrobromate and bromate of potassa, and the former salt is obtained in cubic crystals by evaporation. The bromine may then be set free by means of chlorine, and separated by heat*. M. Balard has subsequently improved the mode of preparation so much, that he now prepares bromine on a larger scale, and sells it in Paris at the very moderate rate of 28 francs an ounce.

According to all the experiments hitherto made, bromine appears to be an element. It is so very similar in most respects to chlorine and iodine, and, in the order of its chemical relations, is so constantly intermediate between them, that M. Balard at first suspected it to be some unknown compound of these substances, and M. Dumas was reported to have discovered such a body possessed of all the properties of bromine. There seems, however, to be no good ground for this assertion; but, on the contrary, an experiment recently performed by M. De la Rive affords a very strong argument against this supposition. He finds that when a compound of bromine and iodine is mixed with starch, and exposed to the influence of galvanism, bromine appears at the positive and iodine at the negative wire, where the starch acquires a blue tint. On making the experiment with bromine containing a little bromide of iodine, the same appearance ensues; but if iodine is not previously added, the starch does not receive a tint of blue.

Bromine is in most cases easily detected by means of chlorine; for this substance displaces bromine from its combination with hydrogen,

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* According to the authorities of Berzelius and Thenard, whose treatises I have consulted, the mode of treating the cubic crystals, (which consist of bromide of potassium, and not hydrobromate of potassa, as stated by Dr Turner) in order to extract the bromine, is to mix them in a small retort, with the peroxide of manganese in powder, and act on the mixture with sulphuric acid, diluted with half its weight of water, with the assistance of heat. The beak of the retort must plunge under cold water. As the distillation proceeds, the bromine passes over in red vapours, and condenses under the water in the form of brown and heavy drops.—*See Berzelius, Traité de Chim.* i. 293.

It is certainly true, that chlorine will disengage bromine from the bromide of potassium, as mentioned by Dr Turner; and it is possible that M. Balard may have recently modified his process in this particular. But supposing this to be the case, it is remarkable, that neither Berzelius nor Henry, in their treatises, both published in 1829, should have alluded to the circumstance. B.

metals, and most other bodies. The appearance of its vapour, or the colour of its solution in ether, will then render its presence obvious.

The combining proportion of bromine has not yet been precisely determined, but judging from M. Balard's analysis of the bromides of potassium and silver, 75 may be assumed as an approximation.

## *Hydrobromic Acid Gas.*

No chemical action takes place between the vapour of bromine and hydrogen gas at common temperatures, not even by the agency of the direct solar rays; but on introducing a lighted candle, or a piece of red-hot iron, into the mixture, combination ensues in the vicinity of the heated body, though without extending to the whole mixture, and without explosion. The combination is readily effected by the action of bromine on some of the gaseous compounds of hydrogen. Thus on mixing the vapour of bromine with hydriodic acid, sulphuretted hydrogen, or phosphuretted hydrogen gas, decomposition ensues, and hydrobromic acid gas is generated. It may be conveniently made for experimental purposes by a process similar to that for forming hydriodic acid. A mixture of bromine and phosphorus, slightly moistened, yields, by the aid of a gentle heat, a large quantity of pure hydrobromic acid gas, which should be collected either in dry glass bottles, or over mercury.

Hydrobromic acid gas is colourless, has an acid taste, and pungent odour. It irritates the glottis powerfully, so as to excite cough, and when mixed with moist air, yields white vapours, which are denser than those occasioned under the same circumstances by muriatic acid gas. It undergoes no decomposition when transmitted through a red-hot tube, either alone, or mixed with oxygen. It is not affected by iodine; but chlorine decomposes it instantly, with production of muriatic acid gas, and deposition of bromine. It may be preserved without change over mercury; but potassium and tin decompose it with facility, the first at common temperatures, and the last by the aid of heat.

Hydrobromic acid gas is very soluble in water. The aqueous solution may be made by treating bromine with sulphuretted hydrogen dissolved in water, or still better, by transmitting a current of hydrobromic acid gas through pure water. The liquid becomes hot during the condensation, acquires great density, increases in volume, and emits white fumes when exposed to the air. This acid solution is colourless when pure, but possesses the property of dissolving a large quantity of bromine, and then receives the tint of that substance.

Chlorine decomposes the solution of hydrobromic acid in an instant. Nitric acid likewise acts upon it, though less suddenly, occasioning the disengagement of bromine, and probably the formation of water and nitrous acid. The nitro-hydrobromic acid is analogous to *aqua regia*, and possesses the property of dissolving gold.

The elements of sulphuric and hydrobromic acids react on each other in a slight degree; and hence on decomposing hydrobromate of potassa by sulphuric acid, the hydrobromic is generally mixed with a little sulphurous acid gas.

Metallic oxides, as might be expected, do not act in a uniform manner on hydrobromic acid. The alkalies, earths, oxides of iron, and peroxides of copper and mercury, form compounds which may be regarded as hydrobromates; whereas the oxide of silver, and protoxide of lead, give rise to double decomposition, in consequence of which water and a metallic bromide result.

The composition of hydrobromic acid gas is easily inferred from the two following facts. 1. On decomposing hydrobromic acid gas by potassium, a quantity of hydrogen remains precisely equal to half the volume of the gas employed; and 2. when hydriodic acid gas is decomposed by bromine, the resulting hydrobromic acid occupies the very same space as the gas which is decomposed. It is hence apparent that hydrobromic is analogous to hydriodic and muriatic acid gases; or, in other words, that 100 measures of hydrobromic acid gas contain 50 measures of the vapour of bromine, and 50 of hydrogen. By weight it may be regarded as a compound of one proportional of each element.

Since bromine decomposes hydriodic, and chlorine hydrobromic acid, it is obvious that bromine, in relation to hydrogen, is intermediate between chlorine and iodine; for it has a stronger affinity for hydrogen than iodine, and a weaker than chlorine. The affinity of bromine and oxygen for hydrogen appears nearly similar; for while oxygen cannot detach hydrogen from bromine, bromine does not decompose watery vapour.

The salts of hydrobromic acid are termed *hydrobromates.* Like the free acid, they are decomposed, and the presence of bromine detected, by means of chlorine. On mixing a soluble hydrobromate with the nitrates of lead, silver, and protoxide of mercury, white precipitates are obtained, which are very similar in appearance to the chlorides of those metals, but which are metallic bromides. On the addition of chlorine, the vapour of bromine is evolved.

## *Bromic Acid.*

The only compound yet known of bromine and oxygen is that formed by the action of pure potassa on bromine, when, by decomposition of water, and the union of its elements with separate portions of bromine, bromic and hydrobromic acids are generated. Of the bromate and hydrobromate of potassa thus produced, the former is much less soluble in water than the latter, and by means of this difference in solubility the two salts are easily separated. The bromate of the other alkalies and alkaline earths may be prepared in a similar manner.

The bromates are analogous to the chlorates and iodates. Thus bromate of potassa is converted by heat into bromide of potassium, with disengagement of pure oxygen gas, deflagrates like nitre when thrown on burning charcoal, and forms with sulphur a mixture which detonates by percussion. The acid of the bromates is decomposed by deoxidizing agents, such as sulphurous acid and sulphuretted hydrogen, in the same manner as the acid of the iodates. The bromates likewise suffer decomposition from the action of hydrobromic and muriatic acids.

Bromate of potassa is said not to precipitate the salts of lead, but to occasion a white precipitate with nitrate of silver, and a yellowish-white with proto-nitrate of mercury; characters which, if correctly observed, distinguish the bromate from the iodate and chlorate of potassa in a very satisfactory manner.

Bromic acid may be procured in a separate state by decomposing a dilute solution of bromate of baryta with sulphuric acid, so as to precipitate the whole of the baryta. The resulting solution of bromic acid may be concentrated by slow evaporation until it acquires the consistence of syrup; but on raising the temperature, in order to expel all the water, one part of the acid is volatilized, and the other resolved into oxygen and bromine. A similar result took place when

the evaporation was conducted into vacuo with sulphuric acid; and accordingly all attempts to procure anhydrous bromic acid have hitherto failed.

Bromic acid has scarcely any odour, but its taste is very acid, though not at all corrosive. It reddens litmus paper powerfully at first, and soon after destroys its colour. It is not affected by nitric or sulphuric acid, except when the latter is highly concentrated, in which case bromine is set free, and effervescence, probably owing to the escape of oxygen gas ensues. From the analysis of bromate of potassa, bromic acid is obviously similar in constitution to iodic, chloric, and nitric acids; that is, consists of one proportion of bromine united with five of oxygen.

*Chloride of Bromine.*—This compound may be formed at common temperatures by transmitting a current of chlorine through bromine, and condensing the disengaged vapours by means of a freezing mixture. The resulting chloride is a volatile fluid of a reddish-yellow colour, much less intense than that of bromine. Its odour is penetrating and causes a discharge of tears from the eyes; and its taste very disagreeable. Its vapour is a deep yellow, like the oxides of chlorine, and enables metals to burn as in an atmosphere of chlorine, doubtless giving rise to the formation of metallic chlorides and bromides.

The chloride of bromine is soluble in water without decomposition; for the solution possesses the colour, odour, and bleaching properties of the compound, and discharges the colour of litmus paper without previously reddening it. By the action of the alkalies it is decomposed, and is converted, by means of the elements of water, into muriatic and bromic acids.

*Bromide of Iodine.*—These substances act readily on each other, and appear capable of uniting in two proportions. The proto-bromide is a solid, convertible by heat into a reddish-brown vapour, which in cooling, condenses into crystals of the same colour, and of a form resembling that of fern leaves. An additional quantity of bromine converts these crystals into a fluid, which in appearance is like a strong solution of iodine in hydriodic acid. This compound dissolves without decomposition in water, but with the alkalies yields hydrobromic and iodic acids.—The existence of two bromides of iodine can scarcely be regarded as satisfactorily established.

*Bromide of Sulphur.*—On pouring bromine on sublimed sulphur, combination ensues, and a fluid of an oily appearance and reddish tint is generated. In odour it somewhat resembles chloride of sulphur, and like that compound emits white vapours when exposed to the air, but its colour is deeper. It reddens litmus paper faintly when dry, but strongly if water is added. Cold water acts slowly upon the bromide of sulphur; but at a boiling temperature, the action is so violent that a slight detonation occurs, and three compounds, hydrobromic and sulphuric acids, and sulphuretted hydrogen are formed. The formation of these substances is of course attributable to decomposition of water, and the union of its elements with bromine and sulphur. Bromide of sulphur is likewise decomposed by chlorine, which unites with sulphur, and displaces bromine.

*Bromide of Phosphorus.*—When bromine and phosphorus are brought into contact in a flask filled with carbonic acid gas, they act suddenly on each other with evolution of heat and light, and two compounds are generated; one a crystalline solid which is sublimed and collects in the upper part of the flask, and the other a fluid, which remains at the bottom. The latter is regarded by M. Balard as a proto-bromide, and the former as a deuto-bromide of phosphorus.

The proto-bromide retains its liquid form even at 52° F. It is readily converted into vapour by heat, and on exposure to the air emits penetrating fumes. It reddens litmus paper faintly, an effect which is probably owing to the presence of moisture. With water it acts energetically and with free disengagement of caloric, hydrobromic acid gas being evolved when only a few drops of water are employed; but if a large quantity is used, the gas is dissolved, and the acid solution leaves by evaporation a residuum, which burns slightly when dried, and is converted into phosphoric acid.

The deuto-bromide is yellow in its solid state; but with gentle heat becomes a red-coloured liquid, which by increase of temperature is converted into vapour of the same tint. On cooling after fusion it yields rhombic crystals; but when its vapour is condensed, the crystals are acicular. It is decomposed by metals, probably with the formation of metallic bromides and phosphurets. It emits dense penetrating fumes on exposure to the air, and with water gives rise to the production of hydrobromic and phosphoric acids.

Chlorine has a greater affinity for phosphorus than bromine, and decomposes both the bromides with evolution of the vapour of bromine. These compounds are not decomposed by iodine; but on the contrary bromine decomposes iodide of phosphorus.

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## SECTION XIV.

### *FLUORINE.*

The substance to which this name is applied has not hitherto been obtained in an insulated form, and therefore the properties which are peculiar to it in that state, are entirely unknown. From the nature of its compounds it appears to belong to the class of negative electrics, and like oxygen and chlorine, to have a powerful affinity for hydrogen and metallic substances. With hydrogen it constitutes a peculiar and very powerful acid, the *hydrofluoric*, the history of which will occupy the greater part of this section.

### *Hydrofluoric Acid.*

This acid was first procured in its pure state in the year 1810 by MM. Gay-Lussac and Thenard, and described in the second volume of their *Recherches Physico-Chimiques.* It is prepared by acting on the mineral called *fluor spar*, carefully separated from siliceous earth and reduced to fine powder, with twice its weight of concentrated-sulphuric acid. The mixture is made in a leaden retort; and on applying heat, an acid and highly corrosive vapour distils over, which must be collected in a receiver of the same metal surrounded with ice. As the materials swell up considerably during the process, owing to a quantity of vapour forcing its way through a viscid mass, the retort should be capacious. At the close of the operation pure hydrofluoric acid is found in the receiver, and the retort contains dry sulphate of lime. The chemical changes are similar to those which occur in the decomposition of chloride of sodium by sulphuric acid, as explained at page 198. Fluor spar consists of fluorine and calcium, and when acted on by oil of vitriol, the water of that acid is resolved

into its elements; the hydrogen uniting with fluorine generates hydrofluoric acid, and the lime, formed by the union of the oxygen of water and calcium, combines with sulphuric acid. If the oil of vitriol is of sufficient strength, all its water is decomposed, and the resulting hydrofluoric acid is anhydrous.

Hydrofluoric acid, at the temperature of 32° F. is a colourless fluid, and remains in that state at 59° if preserved in well stopped bottles; but when exposed to the air, it flies off in dense white fumes, which consist of the acid vapour combined with the moisture of the atmosphere. Its specific gravity is 1.0609; but its density may be increased to 1.25 by gradual additions of water. Its affinity for this liquid far exceeds that of the strongest sulphuric acid, and the combination is accompanied with a hissing noise, as when red-hot iron is quenched by immersion in water.

The vapour of hydrofluoric acid is much more pungent than chlorine or any of the irritating gases. Of all known substances, it is the most destructive to animal matter. When a drop of the concentrated acid of the size of a pin's head comes in contact with the skin, instantaneous disorganization ensues, and deep ulceration of a malignant character is produced. On this account the greatest care is requisite in the preparation of pure hydrofluoric acid.

This acid when concentrated acts energetically on glass. The transparency of the glass is instantly destroyed, caloric is evolved, and the acid boils, and in a short time entirely disappears. A colourless gas, commonly known by the name of *fluosilicic acid gas*, is the sole product. This compound is always formed when hydrofluoric acid comes in contact with siliceous substances. For this reason it cannot be preserved in glass; but must be prepared and kept in metallic vessels. Those of lead, from their cheapness, are often used; but vessels of silver or platinum are preferable. In consequence of its powerful affinity for siliceous matter, hydrofluoric acid may be employed for etching on glass; and when used with this intention, it should be diluted with three or four times its weight of water.

Hydrofluoric acid has all the usual characters of a powerful acid. It has a strong sour taste, reddens litmus paper, and with alkaline substances forms salts, which are termed *hydrofluates*. All these salts are decomposed by strong sulphuric acid with the aid of heat, and the hydrofluoric acid while escaping may be detected by its action on glass.

Hydrofluoric acid acts violently on some of the metals, especially on the bases of the alkalies. Thus when potassium is brought in contact with the concentrated acid, an explosion attended with heat and light ensues; hydrogen gas is disengaged, and a white compound, the fluoride of potassium, is generated. It is a solvent for some elementary principles which resist the action even of nitro-muriatic acid. Thus it dissolves silicium, zirconium, and columbium, with evolution of hydrogen gas; and when mixed with nitric acid, it proves a solvent for silicium which has been condensed by heat, and for titanium. The nitro-hydrofluoric acid, however, is incapable of dissolving gold and platinum. Several oxidized bodies, which are not attacked by sulphuric, nitric, or muriatic acid, are readily dissolved by hydrofluoric acid. As examples of this fact, several of the weaker acids, such as silica or silicic acid, titanic, columbic, molybdic and tungstic acids may be enumerated. (Berzelius.)

Chemists are not agreed as to the precise combining proportion of fluorine. According to the experiments of Dr Thomson, 18 is the true atomic weight of this substance; but as Berzelius has far more practi-

cal knowledge of the compounds of fluorine than other chemists, his result is probably nearer the truth. He found that 100 parts of pure fluoride of calcium prepared with the greatest care, yielded with sulphuric acid 175 parts of sulphate of lime. According to these numbers, fluoride of calcium consists of 20 parts or one proportion of calcium, and 18.86 parts or one proportion of fluorine, giving 38.86 as the equivalent of the compound; and as the constitution of hydrofluoric is analogous to that of muriatic and hydriodic acids, it is composed of 18.86 parts of fluorine and 1 part of hydrogen.

A different view of the compounds of fluorine was originally taken by Gay-Lussac and Thenard, and is still held by some chemists. They adopted the opinion that hydrofluoric acid is a compound of a certain inflammable principle and oxygen, and applied to it the name of *fluoric acid*, previously introduced by Scheele. Fluor spar on this view is a fluate of lime, and when this salt is decomposed by oil of vitriol, the fluoric is merely displaced by the sulphuric acid, and the former passes off combined with the water of the latter. What I have described as anhydrous hydrofluoric acid is, according to this hypothesis, hydrated fluoric acid; and when acted on by potassium, this metal is oxidized at the expense of the water, and potassa thus generated unites with fluoric acid, forming, not fluoride of potassium, but fluate of potassa. The combining proportion of fluoric acid, as inferred from the analysis of Berzelius, is 10.86; for 38.86 parts or one equivalent of fluor spar is supposed to contain 28 parts of lime, (20 calcium and 8 oxygen,) thus leaving 10.86 as the equivalent of the acid.

The theory, according to which fluor spar is a compound of fluorine and calcium, originated as a suggestion with M. Ampère of Paris, and was afterwards supported experimentally by Sir H. Davy. It was found that pure hydrofluoric acid evinces no sign of containing either oxygen or water. Charcoal may be intensely heated in the vapour of the acid without the production of carbonic acid. When hydrofluoric acid was neutralized with dry ammoniacal gas, a white salt resulted, from which no water could be separated; and on treating this salt with potassium, no evidence could be obtained of the presence of oxygen. On exposing the acid to the agency of galvanism, there was a disengagement at the negative pole of a small quantity of gas, which was inferred from its combustibility to be hydrogen; while the platinum wire of the opposite side of the battery was rapidly corroded, and became covered with a chocolate-coloured powder. Sir H. Davy explains these phenomena by supposing hydrofluoric acid to have been resolved into its elements, and that fluorine, at the moment of arriving at the positive side of the battery, entered into combination with the platinum wire which was employed as a conductor. Unfortunately, however, he did not succeed in obtaining fluorine in an insulated state. Indeed, from the noxious vapours that arose during the experiment, it was impossible to watch its progress, and examine the different products with that precision, which is essential to the success of minute chemical inquiries, and which Sir H. Davy has so frequently displayed on other occasions.

Though these researches led to no conclusive result, they afforded so strong a presumption in favour of the opinion of Ampère and Davy, that it was adopted by several other chemists. This view has very recently received strong additional support from the experiments of M. Kuhlman. (Quarterly Journal of Science for July 1827, p. 205.) It was found by this chemist that fluor spar is not in the slightest de-

gree decomposed by the action of anhydrous sulphuric acid, whether at common temperatures or at a red heat. The experiment was made both by transmitting the vapour of anhydrous sulphuric acid over fluor spar heated to redness in a tube of platinum, and by putting the mineral into the liquid acid. In neither case did decomposition ensue; but when the former experiment was repeated with the difference of employing concentrated hydrous instead of anhydrous sulphuric acid, evolution of hydrofluoric acid was produced. M. Kuhlman also transmitted dry muriatic acid gas over fluor spar at a red heat, when hydrofluoric acid was disengaged, without any evolution of hydrogen, and chloride of calcium remained. I am aware of no satisfactory explanation of these facts, except by regarding fluor spar as a compound of fluorine and calcium, and hydrofluoric acid as a compound of fluorine and hydrogen. I shall accordingly adopt this view in the subsequent pages, and never employ the term fluoric acid, except when explaining phenomena according to the theory of Gay-Lussac.

## *Fluoboric Acid Gas.*

The chief difficulty in determining the nature of hydrofluoric acid, arises from the water of the sulphuric acid which is employed in its preparation. To avoid this source of uncertainty, Gay-Lussac and Thenard made a mixture of vitrified boracic acid and fluor spar, and exposed it in a leaden retort to heat, under the expectation that as no water was present, anhydrous fluoric acid would be obtained. In this, however, they were disappointed; but a new gas came over, to which they applied the term of *fluoboric acid gas*. A similar train of reasoning led Sir H. Davy about the same time to the same discovery; though the French chemists had the advantage in priority of publication. Fluoboric acid gas may be prepared more conveniently by mixing one part of vitrified boracic acid, and two of fluor spar, with twelve parts of strong sulphuric acid, and heating the mixture gently in a glass retort. (Dr John Davy, Philos. Trans. for 1812.) When thus prepared, however, it contains fluosilicic acid, according to Berzelius, in considerable quantity; and Dr Thomson detected in it traces of sulphuric acid. The gas may likewise be formed by the action of hydrofluoric acid on a solution of boracic acid.

In the decomposition of fluor spar by vitrified boracic acid, the former and part of the latter undergo an interchange of elements. The fluorine uniting with boron gives rise to fluoboric acid gas; and by the union of calcium and oxygen, lime is generated, which combines with boracic acid, and is left in the retort as borate of lime. The fluoboric acid gas, therefore, is composed of boron and fluorine. Those who adopt the theory of Gay-Lussac give a different explanation, and regard this gas as a compound of fluoric and boracic acids. The lime of fluor spar is supposed to unite with one portion of boracic acid, and fluoric acid at the moment of separation with another, yielding borate of lime and fluoboric acid gas.

Fluoboric acid gas is colourless, has a penetrating pungent odour, and extinguishes flame on the instant. Its specific gravity, according to Dr Thomson, is 2.3622. It reddens litmus paper as powerfully as sulphuric acid, and forms salts with alkalies which are called *fluoborates*. It has a singularly great affinity for water. When it is mixed with air or any gas which contains watery vapour, a dense white cloud appears, which is a combination of water and fluoboric

acid gas. From this circumstance, it affords an exceedingly delicate test of the presence of moisture in gases. Fluoboric acid gas is rapidly absorbed by water. According to Dr John Davy, water absorbs 700 times its volume. Caloric is evolved during the absorption, and the water acquires an increase of volume. The saturated solution is limpid, fuming, and very caustic. On the application of heat, part of the gas is disengaged; but afterwards the whole solution is distilled.

Gay-Lussac and Thenard, and Dr Davy were of opinion that fluoboric acid gas is dissolved by water without decomposition; but Berzelius denies the accuracy of their observation. On transmitting the gas into water until the liquid acquires a sharply sour taste, but is far from being saturated, a white powder begins to subside, and on cooling, a considerable quantity of boracic acid is deposited in crystals. It appears that in a certain state of dilution, part of the fluoboric acid and water mutually decompose each other with formation of boracic and hydrofluoric acids. The latter unites, according to Berzelius, with undecomposed fluoboric acid, forming what he has called the *boro-hydrofluoric acid*. On concentrating the liquid by evaporation, the boracic and hydrofluoric acids decompose each other, and the original compound is reproduced.

Fluoboric acid gas does not act on glass, but attacks animal and vegetable matters with energy, converting them, like sulphuric acid, into a carbonaceous substance. This action is most probably owing to its affinity for water.

When potassium is heated in fluoboric acid gas, the metal takes fire, and a chocolate-coloured solid, wholly devoid of metallic lustre, is formed. This substance is a mixture of fluoride of potassium, and boron; and by the action of water the former is dissolved, and the boron left in a solid state.

The composition of fluoboric acid gas has not hitherto been determined by direct experiment. Dr Davy ascertained that it unites with an equal measure of ammoniacal gas, forming a solid salt; and also combines with twice and three times its volume of ammonia, yielding liquid compounds. In the first salt the relative weights of the constituent gases are in the ratio of their specific gravities; and if the compound consists of one proportion of each, it will be thus constituted,

| | | | |
|---|---|---|---|
| Fluoboric acid gas | 2.3622 | 68.04 | one proportional. |
| Ammoniacal gas | 0.5902 | 17 | one proportional. |

and the combining proportion of the acid may be assumed in round numbers to be 68*. Now supposing this acid to be formed of three proportionals of fluorine and one of boron, its equivalent will be 64.58,

* It is more probable that the first salt consists of two proportionals of the acid combined with one of ammonia. It is a well known fact, that combining weights, or equivalents of the great majority of the gases, whether simple or compound, occupy the same space; while the combining weights of a few, such as ammonia, muriatic acid, deutoxide of nitrogen, have a volume double the usual volume. Now it is most probable that fluoboric acid, in its constitution, conforms to the general rule, and that, therefore, one proportional of it fills but half the space that is occupied by one proportional of ammonia. Admitting this view, a combination of equal volumes of these gases must be a bifluoborate, and the equivalent of fluoboric acid will be only half as great as that given by Dr Turner, or 34.02. B.

a number which approximates to the preceding. But this view is quite hypothetical. Dr Thomson considers 34 as the equivalent of fluoboric acid gas, and believes it to consist of one proportion of fluorine and two of boron. His opinion, however, is very improbable; for the formation of the gas from a mixture of boracic acid and fluor spar, according to this supposition, appears quite inexplicable. These remarks will serve to show that the data for forming an opinion on this subject are uncertain.

## ON THE COMPOUNDS OF THE SIMPLE NON-METALLIC ACIDIFIABLE COMBUSTIBLES WITH EACH OTHER.

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## SECTION I.

### *HYDROGEN AND NITROGEN—AMMONIACAL GAS.*

The *spirit of hartshorn* has been long known to chemists; but the existence of ammonia as a gas was first noticed by Dr. Priestley, and was described by him in his works under the name of *alkaline air.* It is sometimes called the *volatile alkali;* but the terms *ammonia* and *ammoniacal gas* are now more commonly employed.

The most convenient method of preparing ammoniacal gas for the purposes of experiment, is by applying a gentle heat to the concentrated solution of ammonia, contained in a glass vessel. It soon enters into ebullition, and a large quantity of pure ammonia is disengaged.

Ammonia is a colourless gas, which has a strong pungent odour, and acts powerfully on the eyes and nose. It is quite irrespirable in its pure form, but when diluted with air, it may be taken into the lungs with safety. Burning bodies are extinguished by it, nor is the gas inflamed by their approach. Ammonia, however, is inflammable in a low degree. For when a lighted candle is immersed in it, the flame is somewhat enlarged, and tinged of a pale yellow colour at the moment of being extinguished; and a small jet of the gas will burn in an atmosphere of oxygen. A mixture of ammoniacal and oxygen gases detonates by the electric spark; water is formed, and nitrogen remains. A little nitric acid is generated at the same time, except when a smaller quantity of oxygen is employed than is sufficient for combining with all the hydrogen of the ammonia. (Dr. Henry in the Philos. Trans. for 1809.)

Ammoniacal gas at the temperature of 50° F. and under a pressure equal to 6.5 atmospheres, becomes a transparent colourless liquid. It is also liquefied, according to Guyton-Morveau, under the common pressure, by a cold of 70 degrees below zero of Fahrenheit; but there is no doubt that the liquid which he obtained was a solution of ammonia in water.

Ammonia has all the properties of an alkali in a very marked manner. Thus it has an acrid taste, and gives a brown stain to turmeric paper; though the yellow colour soon reappears on exposure to the air, owing to the volatility of the alkali. It combines also with acids, and neutralizes their properties completely. All these salts suffer decomposition by being heated with the fixed alkalies or alkaline earths, such as potassa or lime. These substances unite with the acid of the salt, and the ammonia is expelled. None of the ammoniacal salts can sustain a red heat without being dissipated in vapour or decomposed, a character which manifestly arises from the volatile nature of the alkali. If combined with a volatile acid, such as the

muriatic, the compound itself sublimes unchanged by heat; but if it is in combination with an acid, such as the phosphoric, which is fixed in the fire, the ammonia alone is expelled.

Hydrogen and nitrogen gases do not unite directly, and therefore chemists have no synthetic proof of the constitution of ammonia. Its composition, however, has been determined analytically with great exactness. When a succession of electric sparks is passed through ammoniacal gas, it is resolved into its elements; and the same effect is produced by conducting ammonia through porcelain tubes heated to redness. The late A. Berthollet analyzed ammonia in both ways, and ascertained that 200 measures of that gas, on being decomposed, occupy the space of 400 measures, 300 of which are hydrogen, and 100 nitrogen. Dr Henry has very recently made an analysis of ammonia by means of electricity, and his experiment proves beyond a doubt that the proportions above given are rigidly exact. (Annals of Philosophy, xxiv. 346.)

| | | *Grains.* |
|---|---|---|
| Now since 150 cubic inches of hydrogen weigh | . . | 3.177 |
| 50 nitrogen | . . | 14.826 |
| 100 cubic inches of ammonia must weigh | | 18.003 |

and it is composed by weight of

| | | | |
|---|---|---|---|
| Hydrogen | 3.177 | 3 | or three proportionals. |
| Nitrogen | 14.826 | 14 | or one proportional. |

Its equivalent, therefore, is 17.

The specific gravity of ammonia, according to this calculation, is 0.5902, a number which agrees closely with those ascertained directly by Sir H. Davy and Dr Thomson.

Ammoniacal gas has a powerful affinity for water, and for this reason must always be collected over mercury. Owing to this attraction, a piece of ice, when introduced into a jar full of ammonia, is instantly liquefied, and the gas disappears in the course of a few seconds. Sir H. Davy, in his elements, states that water at 50° F. and when the barometer stands at 29.8 inches, absorbs 670 times its volume of ammonia; and that the solution has a specific gravity of 0.875. According to Dr. Thomson, water at the common temperature and pressure takes up 780 times its bulk. By strong compression water absorbs the gas in still greater quantity. Caloric is evolved during the absorption, and a considerable expansion, independently of the increased temperature, occurs at the same time.

The concentrated solution of ammonia, commonly though incorrectly termed *liquid ammonia*, is made by passing a current of the gas, as long as it continues to be absorbed, into distilled water, which is kept cool by means of ice or moist cloths. The gas may be prepared from any salt of ammonia by the action of any pure alkali or alkaline earth; but muriate of ammonia and lime, from economical considerations, are always employed. The proportions to which I give the preference are equal parts of muriate of ammonia and well-burned quicklime; considerable excess of lime being taken, in order to decompose the muriate more expeditiously and completely. The lime is slaked by the addition of water, and as soon as it has fallen into powder, it should be placed in an earthen pan, and covered to protect it from the carbonic acid of the air, till it is quite cold. It is then mixed in a mortar with the muriate of ammonia, previously reduced to fine powder, and the mixture is put into a retort or other convenient glass vessel. Heat is then applied, and the temperature gradually in-

creased as long as a free evolution of gas continues. The ammonia should be conducted, by means of a Welter's safety tube, into a quantity of distilled water equal to the weight of the salt employed. The residue consists of muriate of lime, or strictly chloride of calcium and lime.

The concentrated solution of ammonia, as thus prepared, is a clear colourless liquid, of specific gravity 0.936. It possesses the peculiar pungent odour, taste, alkalinity, and other properties of the gas itself. On account of its great volatility, it should be preserved in well-stopped bottles, a measure which is also required to prevent the absorption of carbonic acid. At a temperature of 130° F. it enters into ebullition, owing to the rapid escape of pure ammonia; but the whole of the gas cannot be expelled by this means, as at last the solution itself evaporates. It freezes at about the same temperature as mercury.

The following table, from Sir H. Davy's Elements of Chemical Philosophy, shows the quantity of real ammonia contained in 100 parts of solutions of different densities, at 59° F. and when the barometer stands at 30 inches. The specific gravity of water is supposed to be 10,000:—

*Table of the quantity of Real Ammonia in Solutions of different Densities.*

| 100 *parts of sp. gravity* | | *of real Ammonia* | 100 *parts of sp. gravity* | | *of real Ammonia* |
|---|---|---|---|---|---|
| 8750 | contain | 32.5 | 9435 | contain | 14.53 |
| 8875 | . . | 29.25 | 9476 | . . | 13.46 |
| 9000 | . . | 26.00 | 9513 | . . | 12.40 |
| 9054 | . . | 25.37 | 9545 | . . | 11.56 |
| 9166 | . . | 22.07 | 9573 | . . | 10.82 |
| 9255 | . . | 19.54 | 9597 | . . | 10.17 |
| 9326 | . . | 17.52 | 9619 | . . | 9.60 |
| 9385 | . . | 15.88 | 9692 | . . | 9.50 |

The presence of free ammoniacal gas may always be detected by its odour, by its temporary action on the yellow turmeric paper, and by forming dense white fumes, the muriate of ammonia, when a glass rod moistened with muriatic acid is brought near it.

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# SECTION II.

## *COMPOUNDS OF HYDROGEN AND CARBON.*

Chemists have for several years been acquainted with two distinct compounds of carbon and hydrogen, the carburetted hydrogen and olefiant gas; but the researches of Mr Faraday have enriched the science by the discovery of two new substances of a similar nature, and the same able chemist has demonstrated the existence of others, though he has hitherto been unable to obtain them in an insulated form. According to Dr Thomson, naphtha and naphthaline are likewise pure carburets of hydrogen.

## *Light Carburetted Hydrogen.*

This gas is sometimes called *heavy inflammable air*, the *inflammable air of marshes*, *hydro-carburet*, and *proto-carburet of hydrogen*. Dr Thomson proposed the term of *bihydroguret of carbon*; but it is more generally known by the name of *light carburetted hydrogen*. It is formed abundantly in stagnant pools during the spontaneous decomposition of dead vegetable matter; and it may readily be procured by stirring the mud at the bottom of them, and collecting the gas, as it escapes, in an inverted glass vessel. In this state it is found to contain 1-20th of carbonic acid gas, which may be removed by means of lime-water or a solution of pure potassa, and 1-15th or 1-20 of nitrogen. This is the only convenient method of obtaining it.

Light carburetted hydrogen is tasteless and nearly inodorous, and it does not change the colour of litmus or turmeric paper. Water, according to Dr Henry, absorbs about 1-60th of its volume. It extinguishes all burning bodies, and is of course unable to support the respiration of animals. It is highly inflammable, and when a jet of it is set on fire, it burns with a yellow flame, and with a much stronger light than is occasioned by hydrogen gas. With a due proportion of atmospheric air or oxygen gas, it forms a mixture which detonates powerfully with the electric spark, or by the contact of flame. The sole products of the explosion are water and carbonic acid.

Mr Dalton first ascertained the real nature of light carburetted hydrogen, and it has since been particularly examined by Dr Thomson, Sir H. Davy, and Dr Henry. When 100 measures are detonated with rather more than twice their volume of oxygen gas, the whole of the inflammable gas, and precisely 200 measures of the oxygen disappear, water is condensed, and 100 measures of carbonic acid are produced. From this it may be inferred (page 173) that 100 cubic inches of light carburetted hydrogen contain 100 cubic inches of the vapour of carbon and 200 cubic inches of hydrogen gas; and that it is composed by weight of

| | | | |
|---|---|---|---|
| Carbon | . . | 6 | or one proportional. |
| Hydrogen | . . | 2 | or two proportionals. |

Its atomic weight is consequently 8.

From the same data it follows that 100 cubic inches of light carburetted hydrogen, at 60° F, and when the barometer stands at 30 inches, must weigh 16.939 grains, and its specific gravity is therefore 0.5554. This calculated result is almost identical with the specific gravity of the gas as determined directly by Dr Henry and Dr Thomson.

Light carburetted hydrogen is not decomposed by electricity, or by being passed through red-hot tubes, unless the temperature is very great. It may be inferred from the experiments of Berthollet, and from the phenomena that attend the formation of oil gas at high temperatures, that light carburetted hydrogen is resolved into its elements, at least in part, when the heat is very intense. It follows from the nature of the gas, that for each volume so decomposed, two volumes of hydrogen must be set free.

Chlorine and light carburetted hydrogen do not act on each other at common temperatures, when quite dry, even if they are exposed to the direct solar rays. If the gases are moist, and the mixture is kept in a dark place, still no action ensues; but if light be admitted, particularly sunshine, decomposition follows. The nature of the products

depends upon the proportion of the gases. If four measures of chlorine and one of light carburetted hydrogen are present, carbonic and muriatic acid gases will be produced. For during this action, two volumes of chlorine combine with two volumes of hydrogen contained in the carburetted hydrogen, and the other two volumes of chlorine decompose so much water as will likewise give two volumes of hydrogen,—which forms muriatic acid; while the oxygen of the water unites with the carbon, and converts it into carbonic acid. If there are three instead of four volumes of chlorine, carbonic oxide will be generated instead of carbonic acid, because one-half less water will be decomposed. (Dr Henry.) If a mixture of chlorine and light carburetted hydrogen is electrified or exposed to a red heat, muriatic acid is formed, and charcoal deposited.

It was first ascertained by Dr Henry (Nicholson's Journal, vol xix.), and his conclusions have been fully confirmed by the subsequent researches of Sir H. Davy, that the *fire-damp* of coal mines consists almost solely of light carburetted hydrogen. This gas often issues in large quantity from between beds of coal, and by collecting in mines, owing to deficient ventilation, gradually mingles with atmospheric air, and forms an explosive mixture. The first unprotected light which then approaches, sets fire to the whole mass, and a dreadful explosion ensues. These accidents, which were formerly so frequent and so fatal, are now comparatively rare, owing to the employment of the safety lamp; and I conceive it to be demonstrable, on the view that light carburetted hydrogen is the sole constituent of fire-damp, that accidents of the kind cannot occur at all, provided the gauze lamp is in a due state of repair, and employed with the requisite precautions. For this invention we are indebted to Sir H. Davy; and we must in justice remember that it is not, like many discoveries, the offspring of chance, but the fruit of elaborate experiments and close induction; an invention which originated solely with that philosopher, and which may be regarded as one of the happiest efforts of his genius. (Essay on Flame.)

Sir H. Davy, commenced the inquiry by determining the best proportion of air and light carburetted hydrogen for forming an explosive mixture. When the inflammable gas is mixed with three or four times its volume of air, it does not explode at all. It detonates feebly when mixed with five or six times its bulk of air, and powerfully when one to seven or one to eight is the proportion. With 14 times its volume, it still forms a mixture which is explosive; but if a larger quantity of air be admitted, a taper burns in it only with an enlarged flame.

The temperature which is required for causing an explosion was next ascertained. It was found that the strongest explosive mixture may come in contact with iron or other solid bodies heated to redness, or even to whiteness, without detonating, provided they are not in a state of actual combustion; whereas the smallest point of flame, owing to its higher temperature, instantly causes an explosion.

The last important step in the inquiry was the observation that flame cannot pass through a narrow tube. This led Sir H. Davy to the discovery, that the power of tubes in preventing the transmission of flame is not necessarily connected with any particular length; and that a very short one will have the effect, provided its diameter is proportionally reduced. Thus a piece of fine wire gauze, which may be regarded as an assemblage of short narrow tubes, is quite impermeable to flame; and consequently if a common oil lamp be completely surrounded with a cage of such gauze, it may be introduced into an ex-

plosive atmosphere of fire-damp and air, without kindling the mixture. This simple contrivance, which is appropriately termed the *safety-lamp*, not only prevents explosion, but indicates the precise moment of danger. When the lamp is carried into an atmosphere charged with fire-damp, the flame begins to enlarge; and the mixture, if highly explosive, takes fire as soon as it has passed through the gause and burns on its inner surface, while the light in the centre of the lamp is extinguished. Whenever this appearance is observed, the miner must instantly withdraw; for though the flame cannot communicate to the explosive mixture on the outside of the lamp, as long as the texture of the gauze remains entire, yet the heat emitted during the combustion is so great, that the wire, if exposed to it for a few minutes, would suffer oxidation, and fall to pieces.

The peculiar operation of small tubes in obstructing the passage of flame admits of a very simple explanation. Flame is gaseous matter heated so intensely as to be luminous; and Sir H. Davy has shown that the temperature necessary for producing this effect, is far higher than the white heat of solid bodies. Now when flame comes in contact with the sides of very minute apertures, as when wire gauze is laid upon a burning jet of coal gas, it is deprived of so much caloric that its temperature instantly falls below the degree at which gaseous matter is luminous; and consequently, though the gas itself passes freely through the interstices, and is still very hot, it is no longer incandescent. Nor does this take place when the wire is cold only;—the effect is equally certain at any degree of heat which the flame can communicate to it. For since the gauze has a large extent of surface, and from its metallic nature is a good conductor of caloric, it loses heat with great rapidity. Its temperature therefore, though it may be heated to whiteness, is always so far below that of flame, as to exert a cooling influence over the burning gas, and reduce its heat below the point at which it is incandescent.

## *Olefiant Gas.*

This gas was discovered in 1796 by some associated Dutch chemists, who gave it the name of *Olefiant gas*, from its property of forming an oily-like liquid with chlorine. It is sometimes called *bi-carburetted* or *per-carburetted hydrogen* and *hydroguret* of *carbon*; but as none of these terms convey a precise idea of its nature, I shall employ the appellation proposed by its discoverers.

Olefiant gas is prepared by mixing in a capacious retort six measures of strong alcohol with sixteen of concentrated sulphuric acid, and heating the mixture as soon as it is made by means of an Argand lamp. The acid soon acts upon the alcohol, effervescence ensues, and olefiant gas passes over. The chemical changes which take place are of a complicated nature, and the products numerous. At the commencement of the process, the olefiant gas is mixed only with a little ether; but in a short time the solution becomes dark, the formation of ether declines, and the odour of sulphurous acid begins to be perceptible; and towards the close of the operation, though olefiant gas is still the chief product, sulphurous acid is freely disengaged, some carbonic acid is formed, and charcoal in large quantity deposited. The olefiant gas may be collected either over water or mercury. The greater part of the ether condenses spontaneously, and the sulphurous and carbonic acids may be separated by washing the gas with lime-water, or a solution of pure potassa.

The olefiant gas in this process is derived solely from the alcohol; and its production is owing to the strong affinity of sulphuric acid for water. Alcohol is composed of carbon, hydrogen, and oxygen; and from the proportion of its elements, it is inferred to be a compound of 14 parts or one equivalent of olefiant gas, united with 9 parts or one equivalent of water. It is only necessary, therefore, in order to obtain olefiant gas, to deprive alcohol of the water which is essential to its constitution, and this is effected by sulphuric acid. The formation of ether, which occurs at the same time, will be explained hereafter. The other phenomena are altogether extraneous. They almost always ensue when substances derived from the animal and vegetable kingdoms are subjected to the action of sulphuric acid. They occur chiefly at the close of the preceding process, in consequence of the excess of acid which is then present.

Olefiant gas is a colourless elastic fluid, which has no taste, and scarcely any odour when pure. Water absorbs about one-eighth of its volume. Like the preceding compound it extinguishes flame, is unable to support the respiration of animals, and is set on fire when a lighted candle is presented to it, burning slowly with the emission of a dense white light. With a proper quantity of oxygen gas, it forms a mixture which may be kindled by flame or the electric spark, and which explodes with great violence. To burn it completely, it should be detonated with four or five times its volume of oxygen. On conducting this experiment with the requisite care, Dr. Henry finds that for each measure of olefiant gas, precisely three of oxygen disappear, deposition of water takes place, and two measures of carbonic acid are produced. From these data the proportion of its constituents may easily be deduced in the following manner. Two measures of carbonic acid contain two measures of the vapour of carbon, which must have been present in the olefiant gas, and two measures of oxygen. Two-thirds of the oxygen which disappeared are thus accounted for; and the other third must have combined with hydrogen. But one measure of oxygen requires for forming water precisely two measures of hydrogen, which must likewise have been contained in the olefiant gas. It hence follows that 100 cubic inches contain,

| | | *Grains.* |
|---|---|---|
| 200 cubic inches of | the vapour of carbon, which weigh | 25.418 |
| 200 | hydrogen gas, which weigh | 4.236 |

and consequently

| | |
|---|---|
| 100 cubic inches of olefiant gas must weigh - - | 29.654 |

Its specific gravity, accordingly, is 0.9722; whereas its specific gravity, as taken directly by Saussure, is 0.9852; by Henry, 0.967, and by Thomson, 0.97.

Olefiant gas, by weight, consists of

| | | |
|---|---|---|
| Carbon . | 25.418 . | 12, or two proportionals. |
| Hydrogen . | 4.236 . | 2, or two proportionals. |

and its atomic weight is 14.

Olefiant gas, when a succession of electric sparks is passed through it, is resolved into charcoal and hydrogen; and the latter of course occupies twice as much space as the gas from which it was derived. Olefiant gas is decomposed by being passed through red-hot tubes of porcelain. The nature of the products varies with the temperature. By employing a very low degree of heat, it may probably be converted solely into carbon and light carburetted hydrogen; and in this case no increase of volume can occur, because these two gases, for

equal bulks, contain the same quantity of hydrogen. But if the temperature is high, then a great increase of volume takes place, a circumstance which indicates the evolution of free hydrogen, and consequently the total decomposition of some of the olefiant gas.

Chlorine acts powerfully on olefiant gas. When these gases are mixed together in the proportion of two measures of the former to one of the latter, they form a mixture which takes fire on the approach of flame, and which burns rapidly with formation of muriatic acid gas, and deposition of a large quantity of charcoal. But if the gases are allowed to remain at rest after being mixed together, a very different action ensues. The chlorine, instead of decomposing the olefiant gas, enters into direct combination with it, and a yellow liquid like oil is generated. This substance is sometimes called *chloric ether;* but the term *hydrocarburet* of *chlorine,* as indicative of its composition, is more appropriate.

The hydrocarburet of chlorine was discovered by the Dutch chemists; but Dr. Thomson* first ascertained that it is a compound of olefiant gas and chlorine; and its nature has since been more fully elucidated by the researches of MM. Robiquet and Colin.† To obtain it in a pure and dry state, it should be well washed with water, and then distilled from chloride of calcium. As thus purified, it is a colourless volatile liquid, of a peculiar sweetish taste and ethereal odour. Its specific gravity at 45° F. is 1.2201. It boils at 152° F. and may be distilled without change. It suffers complete decomposition when its vapour is passed through a red-hot porcelain tube, being resolved into charcoal, light carburetted hydrogen, and muriatic acid gas.

The composition of the hydrocarburet of chlorine is readily inferred from the fact, that in whatever proportions olefiant gas and chlorine may be mixed together, they always unite in equal volumes. Consequently they combine by weight according to the ratio of their densities; so that the hydrocarburet of chlorine consists of

| | | |
|---|---|---|
| Chlorine | 2.5 | 36, one proportion. |
| Olefiant gas | 0.9722 | 14, one proportion. |
| | 3.4722 | 50 |

and its atomic weight is 50. This estimate is confirmed by the analysis of Robiquet and Colin.

The hydrocarburet of chlorine forms a very dense vapour, its specific gravity, according to Gay-Lussac, being 3.4434. This is so near the united densities of chlorine and olefiant gas, as to leave no doubt that the vapour contains its own volume of each of its constituents.

Dr Henry has demonstrated that light is not essential to the action of chlorine on olefiant gas. On this he has founded an ingenious and perfectly efficacious method of separating olefiant gas from light carburetted hydrogen and carbonic oxide gases, neither of which is acted on by chlorine unless light is present. (Philos. Trans. for 1821.)

Olefiant gas unites also with iodine. This compound was discovered by Mr Faraday (Philos. Trans. for 1821) by exposing olefiant gas and iodine, contained in the same vessel, to the direct rays of the sun. The *hydrocarburet* of *iodine* is a solid white crystalline body, which has a sweet taste and aromatic odour. It sinks rapidly in strong sulphuric acid. It is fused by heat and then sublimed without change, condensing into crystals, which are either tabular or prismatic. On

* Memoirs of the Wernerian Society, vol. i.
† An. de Ch. et de Ph. vol. i. and ii.

exposure to strong heat, it is decomposed, and iodine escapes. It burns, if held in the flame of a spirit lamp, with evolution of iodine and some hydriodic acid. It is insoluble both in water, and in acid or alkaline solutions. Alcohol and ether dissolve it, and on evaporating the solution it crystallizes.

The hydrocarburet of iodine is composed, according to the analysis of Mr Faraday, (Quarterly Journal of Science, vol. xiii.) of

| | | |
|---|---|---|
| Iodine | 124 | or one proportion. |
| Olefiant gas | 14 | or one proportion. |

M. Serullas has also discovered a compound of olefiant gas and iodine. It has a yellow colour like sulphur, and forms scaly crystals of a pearly lustre. Though it differs from the preceding compound in some of its properties, its composition, according to the analysis of M. Serullas, is precisely analogous. (Annales de Ch. et de Ph. vol. xx. and xxii.)

This compound was originally prepared by adding potassium to a solution of iodine in alcohol; but M. Serullas has since made it by mixing a solution of pure potassa in alcohol with an alcoholic solution of iodine. The object of both processes is to present iodine in solution to olefiant gas in a nascent state. It was stated in the section on iodine, that when an alkali, such as potassa, acts on that substance, hydriodic and iodic acids are generated by the decomposition of water. It has been mentioned, also, in the present section, that pure alcohol is a compound of water and olefiant gas. Now, when iodine, potassa, and alcohol, are mixed together, the latter is decomposed :—the water contributes to the formation of iodic and hydriodic acids; while the olefiant gas, instead of assuming the gaseous form, unites with iodine. Potassium acts still more powerfully; because it is converted into potassa at the expense of the water of the alcohol.

*Hydrocarburet of Bromine.*—This compound was formed by M. Serullas by adding one part of the hydrocarburet of iodine to two parts of bromine contained in a glass tube. Instantaneous reaction ensues, attended with disengagement of caloric and a hissing noise, and two compounds, the bromide of iodine and a liquid hydrocarburet of bromine are generated. By means of water the former is dissolved; while the latter, coloured by bromine, collects at the bottom of the liquid. The decoloration is then effected by means of caustic potassa. In order that the process should succeed, the hydrocarburet of iodine must not be in excess.

The hydrocarburet of bromine, after being washed with a solution of potassa, is colourless, heavier than water, very volatile, of a penetrating ethereal odour, and of an exceedingly sweet taste, which it communicates to water in which it is placed, in consequence of being slightly soluble in that liquid. It becomes solid at a temperature between 21° and 23° F. This compound is identical with that which M. Balard formed by letting a drop of bromine fall into a flask full of olefiant gas. (An. de Ch. et Physique, xxxiv.)

## *On the New Carburets of Hydrogen discovered by Mr Faraday*.*

In the process of compressing oil gas in Mr Gordon's apparatus, during which operation the gas is subjected to a force equal to the

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* Philos. Transactions for 1825, Part II. or Annals of Philosophy, xxvii. 44.

pressure of thirty atmospheres, a considerable quantity of liquid collects, which retains its fluidity at the common atmospheric pressure. This liquid, when recently received from the vessel, boils at 60° F. But as soon as the more volatile portions are dissipated, which happens before one-tenth is thrown off, the point of ebullition rises to 100°; and the temperature gradually ascends to 250° before all the liquid is volatilized. This indicated the presence of several compounds, which differ in volatility; and Mr Faraday remarked that the boiling point was more constant between 176° and 190° F. than at any other temperature. He was hence led to search for a definite compound in the fluid which came over at that period; and at length by repeated distillations, and exposing the distilled liquid to a temperature of zero, he succeeded in obtaining a substance to which he has applied the term of *bi-carburet of hydrogen.*

The bi-carburet of hydrogen, at common temperatures, is a colourless transparent liquid, which smells like oil gas, and has also a slight odour of almonds. Its specific gravity is nearly 0.85 at 60° F. At 32° it is congealed, and forms dendritic crystals on the sides of the glass. At zero it is transparent, brittle, and pulverulent, and is nearly as hard as loaf-sugar. When exposed to the air at the ordinary temperature it evaporates, and boils at 186°. The density of its vapour at 60°, and when the barometer stands at 29.98 inches, is nearly 2.7760.

The bi-carburet of hydrogen is very slightly soluble in water, but it dissolves freely in fixed and volatile oils, in ether, and in alcohol, and the alcoholic solution is precipitated by water. It is not acted on by alkalies. It is combustible, and burns with a bright flame and much smoke. When admitted to oxygen gas, so much vapour rises as to make a powerfully detonating mixture. Potassium heated in it does not lose its lustre. On passing its vapour through a red-hot tube, it gradually deposites charcoal, and yields carburetted hydrogen gas. Chlorine, by the aid of sunshine, decomposes it with evolution of muriatic acid. Two triple compounds of chlorine, carbon, and hydrogen, are formed at the same time, one of which is a crystalline solid, and the other a dense thick fluid.

The bi-carburet of hydrogen was analyzed in two ways. In the first, its vapour was passed over oxide of copper heated to redness; and in the second, it was detonated with oxygen gas. Carbonic acid and water were the sole products: and as the absence of oxygen is established by the inaction of potassium, it follows that the bi-carburet consists of carbon and hydrogen only. Mr Faraday infers from his analyses, that 100 measures of the inflammable vapour require 750 of oxygen for complete combustion: that 150 measures of oxygen unite with 300 of hydrogen; and that the remaining 600 combine with 600 of the vapour of carbon, forming 600 measures of carbonic acid gas. Consequently, 100 measures of the vapour are composed of

| | | | | |
|---|---|---|---|---|
| Carbon . | $(0.4166 \times 6)$ . | 2.4996 . | 36 | six proportions. |
| Hydrogen . | $(0.0694 \times 3)$ . | 0.2082 . | 3 | three proportions. |

Its atomic weight is therefore 39; and its specific gravity by calculation, 2.7078.

The second carburet of hydrogen discovered by Mr. Faraday, to which he has not given a name, was derived from the same source as the preceding. It is obtained by heating with the hand the condensed liquid from oil gas, and conducting the vapour which escapes through tubes cooled artificially to zero. A liquid is thus procured, which boils by slight elevation of temperature, and before the thermometer rises to 32° F. is wholly reconverted into vapour,

This vapour is highly combustible, and burns with a brilliant flame. Its specific gravity, at 60° F. and 29.94 of the barometer, is about 1.9065. On being cooled to zero, it is again condensed, and the specific gravity of this liquid at 54°* is 0.627; so that among solids and liquids it is the lightest body known.

Water absorbs the vapour sparingly; but alcohol takes it up in large quantity, and the solution effervesces on being diluted with water. Alkalies and muriatic acid do not affect it. Sulphuric acid, on the contrary, absorbs more than 100 times its volume of the vapour. A dark coloured solution is formed, but no sulphurous acid is disengaged.

From the analysis of this vapour, made by detonating it with oxygen gas, Mr. Faraday infers that each volume requires six of oxygen for complete combustion, and yields four volumes of carbonic acid. It hence follows that 100 measures of the vapour contain 400 measures of the vapour of carbon, and 400 of hydrogen gas, and that this carburet of hydrogen consists, by weight, of

| | | | | |
|---|---|---|---|---|
| Carbon . | $(0.4166 \times 4)$ . | 1.6664 . | 24 . | four proportions. |
| Hydrogen . | $(0.0694 \times 4)$ . | 0.2776 . | 4 . | four proportions. |

Its equivalent is therefore 28. Its specific gravity must be 1.9440; and Mr. Faraday regards this estimate of its specific gravity as nearer the truth than that above stated. The composition of this substance was calculated by Dr. Thomson (Principles of Chemistry, vol. i. p. 151) before the compound itself had been obtained in an insulated form. He terms it *quadro-carburetted hydrogen*, and is of opinion that it exists in sulphuric ether, combined with one equivalent of water. This view is justified by the proportion in which the elements of ether are united.

The discovery of this substance has established a fact which is altogether new to chemists. The elements of the new carburet are united in the proportion of 24 to 4, and those of olefiant gas in that of 12 to 2; that is, the carbon and hydrogen in both are in the ratio of 6 to 1, and therefore each may be regarded as a compound of one atom of its component principles. Hence it appears that two substances may be identical with respect to the proportion of their constituents, and yet be quite distinct in their physical and chemical properties.

This peculiarity is explicable on the supposition that the ultimate atoms of such compounds are differently disposed. It is to be presumed that the smallest possible particle of olefiant gas contains two atoms of carbon and two atoms of hydrogen: and that, in like manner, an integrant particle of the new compound of Mr Faraday contains four atoms of each element. Neither of these substances could, I conceive, be formed by direct union of a single atom of carbon and a single atom of hydrogen. If a combination of the kind were to occur, a new compound, different from any known at present, would be the result. Such appears to me the only satisfactory mode of accounting for the phenomena.

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* This statement seems to require some explanation; as it is not easy to understand how the specific gravity of a liquid, which becomes a vapour at a temperature below 32°, could be ascertained at 54°. The fact is that it was examined in a tube hermetically sealed, and, therefore, under considerable pressure; in consequence of which it retained its liquid form at the temperature above-mentioned. B.

## *Naphtha from Coal Tar.*

This substance is obtained by the distillation of coal tar, and is termed *Naphtha* from its similarity to mineral naphtha. It has a strong and peculiar empyreumatic odour, and is highly inflammable. Potassium may be preserved in it without losing its lustre, which is a sufficient proof that it contains no oxygen. According to Dr. Thomson, one measure of the vapour of naphtha contains six measures of the vapour of carbon, and six of hydrogen gas; or, by weight, consists of 36 or six proportionals of carbon, and 6 or six proportionals of hydrogen.

## *Naphthaline.*

This compound is likewise derived from coal tar. If the distillation is conducted at a very gentle heat, the naphtha, from its greater volatility, first passes over; and afterwards the naphthaline rises in vapour, and condenses in the neck of the retort as a white crystalline solid. (Dr Kid in the Phil. Trans. for 1821, page 216.*)

Pure naphthaline is heavier than water, has a pungent aromatic taste, and a peculiar, faintly aromatic, odour, not unlike that of the narcissus. It is smooth and unctuous to the touch, is perfectly white, and has a silvery lustre. It fuses at 180°, and assumes a crystalline texture in cooling. It volatilizes slowly at common temperatures, and boils at 410° F. Its vapour, in condensing, crystallizes with remarkable facility in thin transparent laminæ.

Naphthaline is not very readily inflamed; but when set on fire it burns rapidly, and emits a large quantity of smoke. It is insoluble in cold, and very sparingly dissolved by hot water. Its proper solvents are alcohol and ether, and especially the latter. It is likewise soluble in olive oil, oil of turpentine, and naphtha.

The alkalies do not act upon naphthaline. The acetic and oxalic acids dissolve it, forming pink coloured solutions. Sulphuric acid enters into direct combination with it, and forms a new and peculiar acid, which Mr Faraday has described in the Philosophical Transactions for 1826, under the name of *Sulpho-naphthalic acid.*

Naphthaline, according to the analysis of Dr Thomson, is a *sesquicarburet of hydrogen;* that is, a compound of 9 parts or an equivalent and a half of carbon, and one equivalent of hydrogen. It is desirable, however, that this analysis should be repeated.

The sulpho-naphthalic acid is made by melting naphthaline with half its weight of strong sulphuric acid, when a red coloured liquid is formed, which becomes a crystalline solid in cooling. The mass is soluble in water, and the solution contains a mixture of sulphuric and sulpho-naphthalic acids. On neutralizing with carbonate of baryta, the insoluble sulphate subsides, while the soluble sulpho-naphthalate remains in solution; and on decomposing this salt by a quantity of sulphuric acid precisely sufficient for precipitating the baryta, pure sulpho-naphthalic acid is obtained.

The aqueous solution of the acid, as thus formed, reddens litmus paper powerfully, and has a bitter acid taste. On concentrating by heat, the liquid at last acquires a brown tint, and if then taken from the

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* See also a paper by Mr Brande in the Quarterly Journal of Science, viii. 289; and Annals of Philosophy, N. S. vi. 136.

fire becomes solid as it cools. If the concentration is effected by means of sulphuric acid in an exhausted receiver, the acid becomes a soft white solid, apparently dry, and at length hard and brittle. In this state it is chemically united with water, deliquesces on exposure to the air, but in close vessels underwent no change during several months. Its taste, besides being bitter and sour, leaves a metallic flavour like that of cupreous salts. When heated in a tube at temperatures below 212°, it is fused without undergoing any other change, and crystallizes from centres in cooling. When more strongly heated, water is expelled, and the acid appears to be then anhydrous; but at the same time it acquires a red tint, and a minute trace of free sulphuric acid may be detected,—circumstances which indicate commencing decomposition. On raising the temperature still higher, the red colour deepens, then passes into brown, and at length the acid is resolved into naphthaline, sulphurous acid, and charcoal; but in order thus to decompose all the acid, a red heat is requisite.

Sulpho-naphthalic acid is readily soluble in water and alcohol, and is also dissolved by oil of turpentine and olive oil, in proportions dependent on the quantity of water which it contains. By the aid of heat it unites with naphthaline. It combines with alkaline bases, and forms neutral salts, which are called *sulpho-naphthalates*. All these salts are soluble in water, and most of them in alcohol, and when exposed to heat in the open air, take fire, leaving sulphates or sulphurets according to circumstances.

From Mr Faraday's analysis of the neutral sulpho-naphthalate of baryta, it appears that 78 parts or one proportional of baryta are combined with 208 parts, or what may be regarded as one equivalent, of sulpho-naphthalic acid. These 208 parts were found to consist nearly of 80 parts or two equivalents of sulphuric acid, 120 parts or twenty equivalents of carbon, and 8 parts or eight equivalents of hydrogen. It has not been demonstrated that sulphuric acid exists as such in the compound, nor is it known how its elements are arranged; but from some interesting facts noticed by Mr Hennel, to be mentioned in the section on ether, it appears very probable that sulpho-naphthalic acid is composed of two proportionals of sulphuric acid, united with twenty of carbon and eight of hydrogen, the two latter existing as a carburet of hydrogen.

## *On Coal and Oil Gas.*

The nature of the inflammable gases derived from the destructive distillation of coal and oil was first ascertained by Dr. Henry*, who showed, in several elaborate and able essays, that these gaseous products do not differ essentially from one another, but consist of a few well known compounds, mixed in different and very variable proportions. The chief constituents were found to be light carburetted hydrogen and olefiant gases, besides which they contain an inflammable vapour, free hydrogen, carbonic acid, carbonic oxide, and nitrogen gases. The discoveries of Mr Faraday have elucidated the subject still further, by proving that there exists in oil gas, and by inference in coal gas also, the vapour of several definite compounds of carbon and hydrogen, the presence of which, for the purpose of illumination, is exceedingly important.

* Nicholson's Journal for 1805. Philosophical Transactions for 1808. Ibid. for 1821.

The illuminating power of the ingredients of coal and oil gas is very unequal. Thus the carbonic oxide and carbonic acid are positively hurtful; that is, the other gases would give more light without them. The nitrogen of course can be of no service. The hydrogen is actually prejudicial; because, though it evolves a large quantity of caloric in burning, it emits an exceedingly feeble light. The carburets of hydrogen are the real illuminating agents, and the degree of light emitted by these is dependent on the quantity of carbon which they contain. Thus olefiant gas illuminates much more powerfully than light carburetted hydrogen; and, for the same reason, the dense vapour of the quadrocarburet of hydrogen emits a far greater quantity of light, for equal volumes, than olefiant gas.

From these facts, it is obvious that the comparative illuminating power of different kinds of coal and oil gas may be estimated, approximately at least, by determining the relative quantities of the denser carburets of hydrogen which enter into their composition. This may be done in three ways. 1, By their specific gravity. 2, By the relative quantities of oxygen required for their complete combustion. 3, By the relative quantity of gaseous matter condensible by chlorine in the dark; for chlorine, when light is excluded, condenses all the hydro-carburets, excepting light carburetted hydrogen. Of these methods, the last I conceive is the least exceptionable*.

The formation of coal and oil gas is a process of considerable delicacy. Coal gas is prepared by heating coal to redness in iron retorts. The quality of the gas, as made at different places, or at the same place at different times, is very variable; the specific gravity of some specimens having been found so low as 0.443, and that of others so high as 0.700. These differences arise in part from the nature of the coal, and partly from the mode in which the process is conducted. The regulation of the degree of heat is the chief circumstance in the mode of operating, by which the quality of the gas is affected. That the quality of the gas may be influenced from this cause is obvious from the fact, that all the dense hydro-carburets are resolved by a strong red heat either into charcoal and light carburetted hydrogen, or into charcoal and hydrogen gas. Consequently the gas made at a very high temperature, though its quantity may be comparatively great, has a low specific gravity, and illuminates feebly. It is, therefore, an object of importance that the temperature should not be greater than is required for decomposing the coal effectually, and that the retorts be so contrived as to prevent the gas from passing over a red-hot surface subsequently to its formation.

These remarks apply with still greater force to the manufacture of oil gas, because oil is capable of yielding a much larger quantity of the heavy hydro-carburets than coal. The quality of oil gas from the same material is liable to such great variation from the mode of manufacture, that the density of some specimens has been found so low as 0.464, and that of others so high as 1.110. The average specific gravity of good oil gas is 0.900, and it should never be made higher. The true interest of the manufacturer is to form as much olefiant gas as possible, with only a small proportion of the heavier hydro-carburets. If the latter predominate, the quantity of gas derived from a given weight of oil is greatly diminished; and a subsequent loss is experi-

* For a discussion of this and other questions relative to oil and coal gas, the reader may consult an essay by Dr Christison and myself in the Edinburgh Philosophical Journal for 1825.

enced by the condensation of the inflammable vapours when the gas is compressed, or while it is circulating through the distributing tubes.

Coal gas, when first prepared, always contains sulphuretted hydrogen, and for this reason must be purified before being distributed for burning. The process of purification consists in passing the gas under strong pressure through milk of lime, or causing it to descend through successive layers of dry hydrate of lime. This latter method, which is practised with great success at Perth under the able direction of Mr Anderson of that city, has this advantage over the former, that while it deprives the gas completely of sulphuretted hydrogen, there is no loss from absorption of olefiant gas or the heavy hydro-carburets, as invariably ensues when milk of lime is employed. But coal gas, after being thus purified, still retains some compound of sulphur, most probably, as Mr Brande conjectures, sulphuret of carbon, owing to the presence of which a minute quantity of sulphurous acid is generated during its combustion. Oil gas, on the contrary, needs no purification; and as it is free from all compounds of sulphur, it does not yield any sulphurous acid in burning, and is therefore better fitted for lighting dwelling-houses than coal gas.

With respect to the relative economy of the two gases, I may observe that the illuminating power of oil gas, of specific gravity 0.900, is about double that of coal gas of 0.600. In coal districts, however, oil gas is fully three times the price of coal gas, and therefore in such situations, the latter is considerably cheaper. (Essay above quoted.)

A successful attempt has been made by Mr Daniell to procure a gas, similar to that from oil in being free from sulphur, but made with cheaper materials. The substance employed for this purpose is a solution of common resin in oil of turpentine. The combustible liquid is made to drop into red-hot retorts in the same manner as oil; and the oil of turpentine, which from its volatility is driven off in vapour, is collected, and again used as a menstruum. For this process Mr Daniell has taken out a patent, and the gas so prepared is employed by Mr Gordon for filling his portable lamps. The gas is reported to be in every respect equal to oil gas; but I have not seen the account of any experiments by which this is proved. The gas made last year, by the late Oil Gas Company of Edinburgh, from resin liquefied by heat, and from a solution of resin in tar, I found to be little superior in illuminating power to good coal gas.

## SECTION III.

### *COMPOUNDS OF HYDROGEN AND SULPHUR—SULPHURETTED HYDROGEN.*

The best method of preparing pure sulphuretted hydrogen is by heating sulphuret of antimony in a retort, or any convenient glass flask, with four or five times its weight of strong muriatic acid. An interchange of elements takes place between water and the sulphuret of antimony, in consequence of which, sulphuretted hydrogen, and the protoxide of antimony, are generated. The former escapes with effervescence, while the latter unites with muriatic acid. The affinities which determine these changes are the attraction of hydrogen for sulphur, of oxygen for antimony, and of muriatic acid for protoxide of antimony. This process may be explained differently. Instead of

water, muriatic acid may be supposed to undergo decomposition, and yielding its hydrogen to the sulphur, and its chlorine to the metal, give rise to sulphuretted hydrogen and chloride of antimony. It is quite doubtful which explanation is the true one, and accordingly some chemists adopt one opinion, and others the other.

Sulphuretted hydrogen is also formed by the action of sulphuric or muriatic acid, diluted with three or four parts of water, on protosulphuret of iron; and the theory of the phenomena is similar to the first of the two explanations just mentioned. Protosulphuret of iron may be procured either by igniting common iron pyrites, (the deuto-sulphuret of iron), by which means one proportional of sulphur is expelled; or by exposing to a low red heat a mixture of two parts of iron filings and rather more than one of sulphur. The materials should be placed in a common earthen or cast iron crucible, and be protected as much as possible from the air during the process. The protosulphuret procured from iron filings and sulphur always contains some uncombined iron, and therefore the gas obtained from it is never quite pure, being mixed with a little free hydrogen. This, however, for many purposes, is quite immaterial.

Sulphuretted hydrogen is a colourless gas, and is distinguished from all other gaseous substances by its offensive taste and odour, which is similar to that of putrefying eggs, or the water of sulphurous springs. Under a pressure of 17 atmospheres, at 50° F, it is compressed into a limpid liquid, which resumes the gaseous state as soon as the pressure is removed.

Sulphuretted hydrogen is very injurious to animal life. According to the experiments of Dupuytren and Thenard, the presence of 1-1500th of sulphuretted hydrogen in air, is instantly fatal to a small bird; 1-800th killed a middle-sized dog, and a horse died in an atmosphere which contained 1-150th of its volume.

Sulphuretted hydrogen extinguishes all burning bodies; but the gas takes fire when a lighted candle is immersed in it, and burns with a pale blue flame. Water and sulphurous acid are the products of its combustion, and sulphur is deposited. With oxygen gas it forms a mixture which detonates by the application of flame or the electric spark. If 100 measures of sulphuretted hydrogen are exploded with 150 of oxygen, the former is completely consumed, the oxygen disappears, water is deposited, and 100 measures of sulphurous acid gas remain. (Dr Thomson.) From the result of this experiment, the composition of sulphuretted hydrogen may be inferred; for it is clear, from the composition of sulphurous acid, (page 179) that two-thirds of the oxygen must have combined with sulphur; and, therefore, that the remaining one-third contributed to the formation of water. Consequently, sulphuretted hydrogen contains its own volume of the vapour of sulphur and of hydrogen gas; and since

| | *Grains.* |
|---|---|
| 100 cubic inches of the vapour of sulphur weigh . | 33.888 |
| 100 cubic inches of hydrogen gas weigh . . . . | 2.118 |
| 100 cubic inches of sulphuretted hydrogen gas must weigh | 36.006 |

and its specific gravity is 1.1805.

The accuracy of this estimate is confirmed by several circumstances. Thus, according to Gay-Lussac and Thenard, the weight of 100 cubic inches of sulphuretted hydrogen is 36.33 grains; and Sir H. Davy and Dr Thomson found it somewhat lighter. When sulphur is heated in hydrogen gas, sulphuretted hydrogen is generat-

ed without any change of volume. On igniting platinum wires in it by the voltaic apparatus, sulphur is deposited, and an equal volume of pure hydrogen remains. A similar effect is produced, though more slowly, by a succession of electric sparks. (Elements of Sir H. Davy, p. 282.) Gay-Lussac and Thenard have given ample demonstration of the same fact. Thus on heating tin in sulphuretted hydrogen gas, a sulphuret of tin is formed; and when potassium is heated in it, vivid combustion ensues, with formation of the sulphuret of potassium. In both cases, pure hydrogen is left, which occupies precisely the same space as the gas from which it was derived. (Recherches Physico-Chimiques, vol. i.)

From the data above stated, it follows that sulphuretted hydrogen is composed, by weight, of

| | | | |
|---|---|---|---|
| Sulphur | 33.888 | 16 | one proportional. |
| Hydrogen | 2.118 | 1 | one proportional. |

Sulphuretted hydrogen has decided acid properties; for it reddens litmus paper, and forms salts with alkalies. It is hence sometimes called *hydrosulphuric* acid. Its salts are termed *hydrosulphurets* or *hydrosulphates*. All the hydrosulphurets are decomposed by muriatic or sulphuric acid, and sulphuretted hydrogen is disengaged with effervescence.

Recently boiled water absorbs its own volume of sulphuretted hydrogen, and acquires the peculiar taste and odour of sulphurous springs. The gas is expelled without change by boiling.

The elements of sulphuretted hydrogen may easily be separated from one another. Thus on putting a solution of sulphuretted hydrogen into an open vessel, the oxygen absorbed from the air gradually unites with the hydrogen of the sulphuretted hydrogen, water is formed, and sulphur deposited. Sulphuretted hydrogen and sulphurous acid mutually decompose each other, with formation of water and deposition of sulphur. If a drachm of fuming nitric acid is poured into a bottle full of sulphuretted hydrogen gas, a bluish-white flame passes rapidly through the vessel, sulphur and nitrous acid fumes make their appearance, and of course water is generated. Chlorine, iodine, and bromine decompose sulphuretted hydrogen, with separation of sulphur, and formation either of muriatic, hydriodic, or hydrobromic acid. An atmosphere charged with sulphuretted hydrogen gas may be purified by means of chlorine in the space of a few minutes.

Sulphuretted hydrogen, from its affinity for metallic substances, is a chemical agent of great importance. It tarnishes gold and silver powerfully, forming with them metallic sulphurets. White paint, owing to the lead which it contains, is blackened by it; and the salts of nearly all the common metals are decomposed by its action. In most cases, the hydrogen of the sulphuretted hydrogen combines with the oxygen of the oxide, and the metal unites with the sulphur.

Sulphuretted hydrogen is readily distinguished from other gases by its odour. The most delicate chemical test of its presence is carbonate of lead (white paint) mixed with water and spread upon a piece of white paper. So minute a quantity of sulphuretted hydrogen may by this means be detected, that one measure of the gas mixed with 20,000 times its volume of air, hydrogen, or carburetted hydrogen, gives a brown stain to the whitened surface. (Dr Henry.)

## *Bisulphuretted Hydrogen.*

Though Scheele discovered this compound, it was first particularly described by Berthollet. (An. de. Chimie, vol. xxv.) It may be made

conveniently by boiling equal parts of recently slaked lime and flowers of sulphur with five or six of water, when a deep orange-yellow solution is formed, which contains a hydrosulphuret of lime with excess of sulphur. On pouring this liquid into strong muriatic acid, copious deposition of sulphur takes place; and the greater part of the sulphuretted hydrogen, instead of escaping with effervescence, is retained by the sulphur. After some minutes, a yellowish semifluid matter like oil collects at the bottom of the vessel, which is *bisulphuretted hydrogen.*

From the facility with which this substance resolves itself into sulphur and sulphuretted hydrogen, its history is imperfect, and in some respects obscure. It is viscid to the touch, and has the peculiar odour and taste of sulphuretted hydrogen, though in a slighter degree. It appears to possess the properties of an acid; for it unites with alkalies and the alkaline earths, forming salts which are termed *sulphuretted hydrosulphurets.* According to Mr Dalton, the bi-sulphuretted hydrogen consists of one equivalent of hydrogen and two equivalents of sulphur; and consequently its combining proportion is 33. This view of its composition is corroborated by Mr Herschel's analysis of the sulphuretted hydrosulphuret of lime. (Edinburgh Philos. Journal, vol. i. p. 13.)

The salts of bisulphuretted hydrogen may be prepared by digesting sulphur in solutions of the alkaline or earthy hydrosulphurets. They are also generated when alkalies or alkaline earths are boiled with sulphur and water; but in this case, another salt is formed at the same time. Thus, on boiling together lime and sulphur, as in the preceding process, the only mode by which sulphuretted hydrogen can be formed at all, is by the decomposition of water; but since no oxygen escapes during the ebullition, it is manifest that the elements of that liquid must have combined with separate portions of sulphur, and have formed two distinct acids. One of these, in all probability, is hyposulphurous acid; and the other is sulphuretted hydrogen.

The salts of bisulphuretted hydrogen absorb oxygen from the air, and pass gradually into hyposulphites. A similar change is speedily effected by the action of sulphurous acid. Dilute muriatic and sulphuric acids produce in them a deposition of sulphur, and evolution of sulphuretted hydrogen gas.

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## SECTION IV.

### *HYDROGEN AND SELENIUM.—HYDROSELENIC ACID.*

Selenium, like sulphur, forms a gaseous compound with hydrogen, which has distinct acid properties, and is termed *seleniuretted hydrogen*, or *hydroselenic acid*. This gas is disengaged when muriatic acid is added to a concentrated solution of any hydroseleniate. It may also be procured by heating the seleniuret of iron in muriatic acid. By decomposition of water, oxide of iron and hydroselenic acid are generated; and while the former unites with muriatic acid, the latter escapes in the form of gas.

Hydroselenic acid gas is colourless. Its odour is at first similar to that of sulphuretted hydrogen; but it afterwards irritates the lining

membrane of the nose powerfully, excites catarrhal symptoms, and destroys for some hours the sense of smelling. It is absorbed freely by water, forming a colourless solution, which reddens litmus paper, and gives a brown stain to the skin. The acid is soon decomposed by exposure to the atmosphere; for the oxygen of the air unites with the hydrogen of the hydroselenic acid, and selenium, in the form of a red powder, subsides.

All the salts of the common metals are decomposed by hydroselenic acid. The hydrogen of that acid combines with the oxygen of the oxide, and a seleniuret of the metal is generated.

Hydroselenic acid gas is composed, according to the analysis of Berzelius, of one equivalent of each of its constituents.

## SECTION V.

### *COMPOUNDS OF HYDROGEN AND PHOSPHORUS.*

Of all the compounds to which chemists have directed their attention, the constitution of none is less perfectly understood than those which form the subject of this section. It has been usual to enumerate two compounds of hydrogen and phosphorus under the names of per and proto-phosphuretted hydrogen, the former being thought to contain a greater proportional quantity of phosphorus than the latter. For the sake of distinction I shall continue to apply these terms in the usual manner; but it will soon appear, that the propriety of the nomenclature is exceedingly doubtful.

*Perphosphuretted Hydrogen.* The gas, to which this name is applied, was discovered in the year 1783 by M. Gengembre, and has since been particularly examined by Mr Dalton, Dr Thomson, M. Dumas, and Professor H. Rose. It may be prepared in several ways. The first method is by heating phosphorus in a strong solution of pure potassa. The second consists in heating a mixture made of small pieces of phosphorus and recently slaked lime, to which a quantity of water is added sufficient to give it the consistence of thick paste. The third method is by the action of dilute muriatic acid, aided by moderate heat, on phosphuret of lime. In these processes, three compounds of phosphorus are generated;—phosphoric acid, hypophosphorous acid, and perphosphuretted hydrogen—all of which are produced by the decomposition of water, and the union of its elements with separate portions of phosphorus. The last method appears to yield the purest gas.

The gas obtained by either of these processes is said by Mr Dalton to be generally, and by M. Dumas to be always, mixed with variable proportions of hydrogen; but Rose denies that free hydrogen gas is evolved, except when the heat is so great as to decompose the hypophosphite, a temperature which is never attained so long as the materials are moist. It has a peculiar odour, resembling that of garlic, and a bitter taste. Its specific gravity, according to Dr Thomson, is 0.9027, according to Dalton 1.1 nearly, and 1.761 according to Dumas. It does not support flame or respiration.

Recently boiled water, according to Dalton, absorbs fully one-eighth of its bulk of this gas, most of which is again expelled by boiling or agitation with other gases; but Dr Thomson states that water

takes up only about five per cent of its volume. The aqueous solution does not redden litmus-paper, nor does the gas itself possess any of the properties of acids. The gas is freely and completely absorbed by a solution of sulphate of copper or chloride of lime, by which means its purity may be ascertained, and the presence of hydrogen detected.

The most remarkable character of this compound, by which it is distinguished from all other gases, is the spontaneous combustion which it undergoes when mixed with air or oxygen gas. If the beak of the retort from which it issues is plunged under water, so that successive bubbles of the gas may arise through the liquid, a very beautiful appearance takes place. Each bubble, on reaching the surface of the water, bursts into flame, and forms a ring of dense white smoke, which enlarges as it ascends, and retains its shape, if the air is tranquil, until it disappears. If received in a vessel of oxygen gas, the entrance of each bubble is instantly followed by a strong concussion, and a flash of white light of extreme intensity. The product of the combustion in both cases is phosphoric acid and water. Mr Dalton observed that it may be mixed with pure oxygen in a tube of three-tenths of an inch in diameter without taking fire; but the mixture detonates when an electric spark is transmitted through it.

In consequence of the combustibility of phosphuretted hydrogen, it would be hazardous to mix it in any quantity with air or oxygen gas in close vessels. For the same reason care is necessary in the formation of this gas, lest, in mixing with the air of the apparatus, an explosion ensue, and the vessel burst. The chance of such an accident is avoided, when phosphuret of lime is used, by filling the flask or retort entirely with dilute acid; and in either of the other processes, by causing the phosphuretted hydrogen to be formed slowly at first, in order that the oxygen gas within the apparatus may be gradually consumed. A very simple method of averting all danger has been lately mentioned to me by Mr Graham. It consists in moistening the interior of the retort with one or two drops of ether, the vapour of which, when mixed with atmospheric air even in small proportion, effectually prevents the combustion of phosphuretted hydrogen.

Perphosphuretted hydrogen gas is resolved into its element by exposure to strong heat, or by successive sparks of electricity; and when sulphur is volatilized in this gas, the phosphuretted is converted into sulphuretted hydrogen. Dr Thomson states that the pure hydrogen in the former case, and in the latter the sulphuretted hydrogen, retain precisely the same volume as the gas from which they were derived. He hence infers that the phosphuretted hydrogen contains its own volume of hydrogen gas; but this fact is disputed by other chemists, and particularly by M. Dumas, who finds that 100 measures of the former contain 150 of the latter. (An. de Ch. et Phy. xxxi. 153.) The quantity of oxygen required to effect the complete combustion of phosphuretted hydrogen, that is, to convert it into water and phosphoric acid, is also uncertain. Dalton and Dumas agree in the opinion that phosphuretted hydrogen requires twice its volume for this purpose; while Dr Thomson states that only one and a half times its volume are requisite.

When perphosphuretted hydrogen is allowed to stand for a few days over water, it deposites part of its phosphorus without change of volume, and ceases to be spontaneously combustible when mixed with atmospheric air. According to Dr Thomson the perphosphuretted hydrogen parts with 1-4th of its phosphorus under these circumstances, and a peculiar gas, which he has called *sub-phosphuretted hydrogen*,

is generated; but M. Dumas maintains that 1-3d of the phosphorus is deposited, and that the new gas is identical with protophosphuretted hydrogen.

Perphosphuretted hydrogen, according to Dr Thomson, is composed of 1 part of hydrogen to 12 of phosphorus; the proportion as stated by Rose is as 1 to 10.52; and according to Dumas, it is as 1 to 16.1. Such results, it is manifest, prove nothing but the uncertainty of our chemical knowledge relative to this subject. They likewise justify the doubt formerly expressed of the constitution of phosphoric and phosphorous acids, as stated by Dr Thomson, (page 187); for his opinion is founded on his experiments on perphosphuretted hydrogen gas.

*Protophosphuretted Hydrogen.* The compound hitherto known by this name was discovered in 1812 by Sir H. Davy. It is a colourless gas, of a disagreeable odour, though less fetid than the foregoing. Water absorbs about one-eighth of its volume. It does not take fire spontaneously when mixed with air or oxygen gas at common temperatures; but the mixture detonates with the electric spark, or when heated to 300° F. Admitted into a vessel of chlorine, it inflames instantly and emits a white light, a property which it possesses in common with perphosphuretted hydrogen. Its specific gravity is estimated by Dr Thomson at 0.9722; but M. Dumas found it to be 1.214.

This gas was prepared by Sir H. Davy by exposing to heat in a retort the solid hydrate of phosphorous acid, (page 189); and the same gas is evolved by treating the hydrous hypophosphorous acid in the same manner. It is also formed, according to Dumas, by the action of concentrated muriatic acid on phosphuret of lime; and likewise by the spontaneous decomposition of perphosphuretted hydrogen gas.

Dr Thomson states that when sulphur is heated in 100 measures of protophosphuretted hydrogen gas, sulphuret of phosphorus, and 200 measures of sulphuretted hydrogen are generated; and he hence infers, that the protophosphuretted hydrogen contains twice its volume of hydrogen gas. Dumas, however, declares that, like perphosphuretted hydrogen, it contains one and a half times its volume of hydrogen. According to both chemists it requires twice its volume of oxygen gas for converting its elements into phosphoric acid and water. The proportion of its elements is said by Dr Thomson to be 1 part of hydrogen to 6 of phosphorus; while according to Dumas the ratio is as 1 to 10.79.

The uncertainty existing with respect to the composition of this compound, has been much increased by a statement made by Rose in his late essay on the combinations of phosphorus, and supported by numerous experiments. (Poggendorff's Annalen, viii. 192). He declares that the gas evolved during the decomposition of hydrated phosphorous acid by heat, though hitherto regarded as protophosphuretted hydrogen, contains a larger proportional quantity of phosphorus than the perphosphuretted hydrogen. One specimen was composed of 1 part of hydrogen to 21 of phosphorus; but the constitution of the gas is variable, according as the heat is applied slowly or rapidly. A similar compound is formed, according to Rose, during the decomposition by heat of hypophosphorous acid.

## SECTION VI.

### *COMPOUNDS OF NITROGEN AND CARBON.*

### *Bicarburet of Nitrogen, or Cyanogen Gas.*

Cyanogen gas, the discovery of which was made in 1815 by M. Gay-Lussac, (Annales de Chimie, vol. xcv.) is prepared by heating the cyanuret of mercury, carefully dried, in a small glass retort, by means of a spirit lamp. This cyanuret, which, on the supposition of its being a compound of the oxide of mercury and prussic acid, was formerly called *prussiate of mercury*, is in reality composed of metallic mercury and cyanogen. On exposing it to a low red heat, it is resolved into its elements. The cyanogen passes over in the form of gas, and the metallic mercury is sublimed. The retort, at the close of the process, contains a small residue of charcoal, derived from the cyanogen itself, a portion of which is decomposed by the temperature employed in its formation; but Gay-Lussac states that no free nitrogen is disengaged till towards the close of the process.

Cyanogen gas is colourless, and has a strong pungent and very peculiar odour. At the temperature of 45° F. and under a pressure of 3.6 atmospheres, it is a limpid liquid, which resumes the gaseous form when the pressure is removed. It extinguishes burning bodies; but it is inflammable, and burns with a beautiful and characteristic purple flame. It can support a strong heat without decomposition. Water, at the temperature of 60° F, absorbs 4.5 times, and alcohol 23 times its volume of the gas. The aqueous solution reddens litmus paper; but this effect is not to be ascribed to the gas itself, but to the presence of acids which are generated by the mutual decomposition of cyanogen and water*.

The composition of cyanogen may be determined by mixing that gas with a due proportion of oxygen, and inflaming the mixture by electricity. Gay-Lussac ascertained in this way that 100 measures of cyanogen require 200 of oxygen for complete combustion, that no water is formed, and that the products are 200 measures of carbonic acid gas and 100 of nitrogen. Hence it follows that cyanogen contains its own bulk of nitrogen, and twice its volume of the vapour of carbon. Consequently, since

| | Grains. |
|---|---|
| 100 cubic inches of nitrogen gas weigh . . | 29.652 |
| 200 the vapour of carbon weigh . | 25.418 |
| 100 cubic inches of cyanogen gas must weigh . | 55.070 |

And it consists by weight of

| | | | |
|---|---|---|---|
| Nitrogen . | 29.652 . | 14 . | one equivalent. |
| Carbon . | 25.418 . | 12 . | two equivalents. |

The specific gravity of a gas so constituted is 1.8054; whereas Gay-Lussac found it, by weighing, to be 1.8064.

Cyanogen, from this view of its composition, is a *bicarburet* of ni-

* Vauquelin, in the Annales de Ch. et de Ph. vol. ix.; or Annals of Philosophy, vol. xiii.

*trogen;* but for the sake of convenience I shall employ the term *cyanogen*, proposed by its discoverer*. All the compounds of cyanogen, which are not acid, are called *cyanurets* or *cyanides*.

Cyanogen, though a compound body, has a remarkable tendency to combine with elementary substances. Thus it is capable of uniting with the simple non-metallic bodies, and evincing a strong attraction for metals. When potassium, for instance, is heated in cyanogen gas, such an energetic action ensues, that the metal becomes incandescent, and a cyanuret of potassium is generated. The affinity of cyanogen for metallic oxides, on the contrary, is comparatively feeble. It enters into direct combination with a few alkaline bases only, and these compounds are by no means permanent. From these remarks it is apparent that cyanogen has no claim to be regarded as an acid.

## *Hydrocyanic or Prussic Acid.*

Prussic acid was discovered in the year 1782 by Scheele, and Berthollet afterwards ascertained that it contains carbon, nitrogen, and hydrogen; but Gay-Lussac first procured it in a pure state, and by the discovery of cyanogen was enabled to determine its real nature. The substance prepared by Scheele was merely a solution of prussic acid in water.

Pure hydrocyanic or prussic acid may be prepared by heating cyanuret of mercury in a glass retort with two-thirds of its weight of concentrated muriatic acid. By an interchange of elements similar to that which was explained in the first process for forming sulphuretted hydrogen (p. 243), the cyanogen of the cyanuret unites with the hydrogen either of water or muriatic acid, forming hydrocyanic acid; while a solution of corrosive sublimate remains in the retort. The vapour of hydrocyanic acid, as it rises, is mixed with moisture and muriatic acid. It is separated from the latter by being conducted through a narrow tube over fragments of marble, with the lime of which the muriatic acid unites. It is next dried by means of the chloride of calcium, and is subsequently collected in a tube surrounded with ice or snow.

Vauquelin proposes the following process as affording a more abundant product than the preceding. It consists in filling a narrow tube, placed horizontally, with fragments of the cyanuret of mercury, and causing a current of sulphuretted hydrogen gas to pass slowly along it. The instant that gas comes in contact with the cyanuret, double decomposition ensues, and hydrocyanic acid and a black sulphuret of mercury are generated. The progress of the sulphuretted hydrogen along the tube may be distinctly traced by the change of colour, and the experiment may be closed as soon as the whole of the cyanuret has become black. It then only remains to expel the hydrocyanic acid by a gentle heat, and collect it in a cool receiver. This process is elegant, easy of execution, and productive.

Pure hydrocyanic acid is a limpid colourless fluid, of a strong odour, similar to that of peach-blossoms. It excites at first a sensation of coolness on the tongue, which is soon followed by heat; but when diluted, it has the flavour of bitter almonds. Its specific gravity at 45° F. is 0.7058. It is so exceedingly volatile, that its vapour during warm weather may be collected over mercury. Its point of ebullition

* From κύανος, *blue*, and γεννάω, *I generate;* because it is an essential ingredient of Prussian blue.

a 79° F, and at zero it congeals. When a drop of it is placed on a piece of glass, it becomes solid; because the cold produced by the evaporation of one portion is so great as to freeze the remainder. It unites with water and alcohol in every proportion.

Pure hydrocyanic acid is a powerful poison, producing in poisonous doses insensibility and convulsions, which are speedily followed by death. A single drop of it placed on the tongue of a dog causes death in the course of a very few seconds; and small animals, when confined in its vapour, are rapidly destroyed. On inspiring the vapour, diluted with atmospheric air, headach and giddiness supervene; and for this reason the pure acid should not be made in close apartments during warm weather. The distilled water from the leaves of the *Prunus lauro-cerasus* owes its poisonous quality to the presence of this acid. Its effects are best counteracted by diffusible stimulants, and of such remedies, solution of ammonia appears to be the most beneficial.

Pure hydrocyanic acid, even when excluded from air and moisture, is very liable to spontaneous changes, owing to the tendency of its elements to form new combinations. These changes sometimes commence within an hour after the acid is made, and it can rarely be preserved for more than two weeks. The commencement of decomposition is marked by the liquid acquiring a reddish-brown tinge. The colour then gradually deepens, a matter like charcoal subsides, and ammonia is generated. On analyzing the black matter, it was found to contain carbon and nitrogen. The acid may be preserved for a longer period if diluted with water, but even then it undergoes gradual decomposition.

Hydrocyanic acid reddens litmus paper feebly, and unites with most alkaline bases, forming salts which are termed *prussiates* or *hydrocyanates*. It is a weak acid; for it does not decompose the carbonates, and no quantity of it can destroy the alkaline reaction of potassa. Its salts are poisonous; they are all decomposed by carbonic acid, and have the odour of hydrocyanic acid, a character by which the hydrocyanates may easily be recognised.

Hydrocyanic acid is resolved by galvanism into hydrogen and cyanogen, the former of which appears at the negative, and the latter at the positive pole. When its vapour is conducted through a red-hot porcelain tube, partial decomposition ensues. Charcoal is deposited, and nitrogen, hydrogen, and cyanogen gases are set at liberty; but the greater part of the acid passes over unchanged. Electricity produces a similar effect. The vapour of hydrocyanic acid takes fire on the approach of flame; and with oxygen gas it forms a mixture which detonates with the electric spark. The products of the combustion are nitrogen, water, and carbonic acid.

The composition of hydrocyanic acid is shown by the following simple but decisive experiment of Gay-Lussac. If a quantity of potassium, precisely sufficient for absorbing 50 measures of pure cyanogen gas, is heated in 100 measures of hydrocyanic acid vapour, the cyanuret of potassium is generated, a diminution of 50 measures takes place, and the residue is pure hydrogen. From this it appears, that hydrocyanic acid vapour is composed of equal volumes of cyanogen and hydrogen, united without any condensation; and, consequently, these two gases combine, by weight, according to the ratio of their densities. The composition of hydrocyanic acid may, therefore, be thus stated:

| | *By Volume.* | *By Weight.* | |
|---|---|---|---|
| Cyanogen | 50 . . | 1.8054 | 26, one equivalent. |
| Hydrogen | 50 . . | 0.0694 | 1, one equivalent. |
| | 100 acid vapour. | | |

The atomic weight of hydrocyanic acid is 27. The specific gravity of its vapour is, of course, intermediate between that of its constituents, or 0.9374: as determined directly by Gay-Lussac, its density is 0.9476.

From the powerful action of hydrocyanic acid on the animal economy, this substance, in a diluted form, is sometimes employed in medical practice to diminish pain and nervous irritability. It may be procured of any given strength by dissolving cyanuret of mercury in water, and transmitting a current of sulphuretted hydrogen gas through the solution till the whole of the cyanuret is decomposed. The decomposition is known to be complete by the filtered liquid remaining colourless and transparent, when mixed with a solution of sulphuretted hydrogen; for should any undecomposed cyanuret of mercury be present, a black precipitate, which is a sulphuret of mercury, will be formed. This test of the complete decomposition of the cyanuret of mercury should never be neglected. The excess of sulphuretted hydrogen is removed by agitation with carbonate of lead, and the hydrocyanic acid is then separated from the insoluble matter by filtration. The process adopted at Apothecaries' Hall in London, is to mix in a retort one part of the cyanuret of mercury, one part of muriatic acid of specific gravity 1.15, and six parts of water; and to distil the mixture until a quantity of acid, equal to that of the water employed, is collected. The product has a density of 0.995. (Brande's Manual of Chemistry, vol. i.) In this process, a little muriatic acid is apt to pass over into the recipient, and render the product impure. Its presence, in a medical point of view, cannot be very material; but it may be separated by mixing the impure acid with a little chalk, and distilling to dryness. The muriatic acid unites with lime, and is retained in the retort, where it may be detected by its appropriate test. Muriatic when mixed with hydrocyanic acid cannot be detected by nitrate of silver; because cyanuret of silver is very similar to the chloride, both in its appearance and in several of its leading properties.

The quality of dilute hydrocyanic acid, however prepared, is very variable, owing to the volatility of the acid, and its tendency to spontaneous decomposition. On this account, it should be made only in small quantities at a time, kept in well-stopped bottles, and excluded from light. The best way of estimating the strength of any solution is that proposed by Dr Ure. To 100 grains, or any other convenient quantity of the acid, contained in a phial, small quantities of the peroxide of mercury in fine powder are successively added, till it ceases to be dissolved. The weight of the peroxide which is dissolved, divided by four, gives the quantity of real hydrocyanic acid present. (Quarterly Journal, vol. xiii.)

The presence of free hydrocyanic acid is easily recognised by its odour. Chemically it may be detected by agitating the fluid supposed to contain it with the peroxide of mercury in fine powder. Double decomposition ensues, by which water and the cyanuret of mercury are generated; and on evaporating the solution slowly, the latter is obtained in the form of crystals.

A test of far greater delicacy, originally noticed by Scheele, is the following. To the liquid supposed to contain hydrocyanic acid add

a solution of green vitriol, throw down the protoxide of iron by a slight excess of pure potassa, and after exposure to the air for four or five minutes, acidulate with muriatic or sulphuric acid, so as to redissolve the precipitate. Prussian blue will then make its appearance, if prussic acid had been originally present. The nature of the chemical change will be explained in the section on the salts of ferrocyanic acid, when describing the manufacture of Prussian blue. M. Lassaigne, who has written an essay on the tests of this acid, (An. de Ch. et Ph. xxvii. 200,) speaks of the *per*sulphate as the proper reagent for this experiment; but according to my observation, the presence of the protoxide is essential to its success. If the iron is strictly at its maximum of oxidation, Prussian blue will not be formed at all, as was proved long ago by Scheele and Proust.

As hydrocyanic acid is sometimes administered with criminal designs, the chemist may be called on to search for its presence in the stomach after death. This subject has been investigated experimentally by MM. Leuret and Lassaigne, and the process they have recommended is the following. The stomach or other substances to be examined are cut into small fragments, and introduced into a retort along with water, the mixture being slightly acidulated with sulphuric acid. The distillation is then conducted at a temperature of 212° F, the volatile products collected in a receiver surrounded with ice, and the presence of hydrocyanic acid in the distilled matter, tested by the method above mentioned. These gentlemen found, that prussic acid may be thus detected two or three days after death; but not after a longer period. The disappearance of the acid appears owing partly to its volatility, and partly to the facility with which it undergoes spontaneous decomposition. (Journal de Chimie Medicale, &c. xii. p. 561.)

## *Cyanic Acid.*

Chemists are acquainted with two acid compounds of cyanogen and oxygen; and it is remarkable, that though the properties of these acids are quite different, their elements, according to the best analyses we possess, are united in the same proportion. That two or more different substances may be composed of the same elements combined in the same ratio, is a fact which can hardly be questioned. (Page 239.) But since examples of the kind are as yet exceedingly rare, it will be proper, before admitting this similarity of composition in the present instance, to suspend our judgment till the analysis of the two cyanic acids shall have been repeated and confirmed by other chemists. In the mean time, however, I shall describe each under the term of *cyanic acid.*

*Cyanic acid* of M. Wöhler. It was stated by Gay-Lussac in the essay already quoted, that cyanogen gas is freely absorbed by pure alkaline solutions; and he expressed the opinion that the alkali combines directly with the cyanogen. It appears, however, from the experiments of M. Wöhler, that, by decomposition of water, hydrocyanic and cyanic acids are formed under these circumstances; and, consequently, that alkaline solutions act upon cyanogen in the same manner as on chlorine, iodine, bromine, and sulphur. But the salts of cyanic acid cannot conveniently be procured in this way, owing to the difficulty of separating the cyanate from the hydrocyanate with which it is accompanied. M. Wöhler finds that the cyanate of potassa may be procured in large quantity by mixing ferrocyanate of potassa with an equal weight of peroxide of manganese in fine powder, and

exposing the mixture to a low red heat. The cyanogen of the ferrocyanic acid receives oxygen from the manganese, and is converted into cyanic acid, which unites with the potassa. The ignited mass is then boiled in alcohol of 86 per cent; and as the solution cools, the cyanate is deposited in small tabular crystals like chlorate of potassa. The only precaution necessary in this process is to avoid too high a temperature.

Cyanic acid is characterized by the facility with which it is resolved by water into carbonic acid and ammonia. This change is effected merely by boiling an aqueous solution of cyanate of potassa; and it takes place still more rapidly when an attempt is made to decompose the cyanate by means of another acid. If the acid is diluted, cyanic acid is instantly decomposed, and carbonic acid escapes with effervescence. But, on the contrary, if a concentrated acid is employed, then the cyanic acid resists decomposition for a short time, and emits a strong odour of vinegar. According to M. Liebig, the acid may be obtained in a free state by transmitting sulphuretted hydrogen gas through water, in which cyanate of silver is suspended; but the operation should be discontinued before all the cyanate is decomposed, since otherwise the free sulphuretted hydrogen would react on the cyanic acid, and effect its decomposition. The acid thus formed is permanent only for a few hours. (An. de Ch. et de Ph. xxxiii. 207.)

Cyanic acid forms a soluble salt with baryta, but insoluble ones with the oxides of lead, mercury, and silver. If the cyanate of potassa is quite pure, it gives a white precipitate with nitrate of silver, and the cyanate of silver so formed dissolves without residue in dilute nitric acid.

Cyanic acid, according to the analysis of M. Wöhler, is composed of 26 parts or one equivalent of cyanogen, and 8 parts or one equivalent of oxygen. (Annales de Chimie et de Physique, vol. xx. and xxvii.) M. Liebig attempted to prove that cyanic acid consists of one equivalent of cyanogen and half an equivalent of oxygen; and contended that it should be called *cyanous acid;* but M. Wöhler has repeated his own analysis, and confirmed his former result. Its accuracy has since been admitted by M. Liebig, who was led into error by the employment of impure materials.

The existence of cyanic acid was suspected by M. Vauquelin before it was actually discovered by Wöhler. The experiments of the former chemist led him to the opinion that a solution of cyanogen in water is gradually converted into hydrocyanic, cyanic, and carbonic acids, and ammonia; and he supposed alkalies to produce a similar change. He did not establish the fact, however, in a satisfactory manner. (An. de Ch. et de Ph. vol. ix.)

*Cyanic acid* of M. Liebig. A powerfully detonating compound of mercury was described in the Philosophical Transactions for 1800 by Mr E. Howard. It is prepared by dissolving 100 grains of mercury in a measured ounce and a half of nitric acid of specific gravity 1.3; and adding, when the solution has become cold, two ounces by measure of alcohol, the density of which is 0.849. The mixture is then heated till a moderately brisk effervescence takes place, during which the fulminating compound is generated. A similar substance may be made by treating silver in the same manner. The conditions necessary for forming these compounds are, that the silver or mercury be dissolved in a fluid which contains so much free nitric acid and alcohol, that on the application of heat, nitric ether shall be freely disengaged.

Fulminating silver and mercury bear the heat of 212° or even 260° F. without detonating; but a higher temperature, or slight percussion be-

tween two hard bodies, causes them to explode with violence. The nature of these compounds was discovered in 1823 by M. Liebig*, who demonstrated that they are salts composed of a peculiar acid, which he termed *fulminic acid*, in combination with the oxide of mercury or silver. According to an analysis of fulminating silver made by MM. Liebig and Gay-Lussac†, the acid of the salt is composed of 26 parts or one proportional of cyanogen, and 8 parts or one proportional of oxygen. It is therefore a real *cyanic acid*, and its salts may with propriety be termed *cyanates*. The fulminating silver is a cyanate of the oxide of silver; and is found to contain one proportional of each element.

It is remarkable that the oxide of silver cannot be entirely separated from cyanic acid by means of an alkali. On digesting cyanate of silver in potassa, for example, one equivalent of the oxide of silver is separated, and a double cyanate is formed, which consists of two equivalents of cyanic acid, one equivalent of the oxide of silver, and one equivalent of potassa. Similar compounds may be procured by substituting other alkaline substances, such as baryta, lime, or magnesia, for the potassa. These double cyanates are capable of crystallizing; and they all possess detonating properties.

From the presence of the oxide of silver in the double cyanates, it was at first imagined that this oxide actually constitutes a part of the acid; but since several other substances, such as the oxides of mercury, zinc, and copper, may be substituted for that of silver, this view can no longer be admitted.

Cyanic acid has not hitherto been obtained in an insulated form; for while some acids do not decompose the cyanates, others act on the cyanic acid itself, and give rise to new products. Muriatic acid, for example, causes the formation of hydrocyanic acid, and a new acid containing chlorine, carbon, and nitrogen, the nature of which has not been determined. Hydriodic acid acts in a similar manner; and a peculiar acid is likewise produced by the action of sulphuretted hydrogen. From subsequent researches, M. Liebig suspects that this acid is composed of sulphur, cyanogen, and oxygen, in the ratio of two equivalents of the first substance, one of the second, and one of the third; but the accuracy of this view has not been demonstrated in a conclusive manner.

## *Cyanuret of Chlorine.*

The existence of this compound was first noticed by Berthollet, who named it *oxy-prussic acid*, on the supposition of its containing prussic acid and oxygen; and it was afterwards described by Gay-Lussac, in his essay on cyanogen, under the appellation of *chlorocyanic acid*. It was procured by this chemist by transmitting chlorine gas into an aqueous solution of hydrocyanic acid until the liquid acquired bleaching properties, removing the excess of chlorine by agitation with mercury, and then heating the mixture, so as to expel the gaseous cyanuret of chlorine. The chemical changes which take place during this process are complicated. At first the elements of hydrocyanic acid unite with separate portions of chlorine, and give rise to muriatic acid and cyanuret of chlorine; and when heat is applied, the elements of the cyanuret and water react on each other, in consequence of which muriatic acid, ammonia and carbonic acid are

* An. de Ch. et de Ph. vol. xxiv. † Ibid. xxv.

generated. Owing to this circumstance, the cyanuret of chlorine was always mixed with carbonic acid, and its properties imperfectly understood.

During the course of last year, M. Serullas succeeded in procuring this compound in a pure state, by exposing cyanuret of mercury, in powder and moistened with water, to the action of chlorine gas contained in a well stopped phial. The vessel is kept in a dark place; and after ten or twelve hours the colour of the chlorine is no longer perceptible, bichloride of mercury is found at the bottom of the phial, and its space is filled with the vapour of cyanuret of chlorine. The bottle is then cooled down to zero by freezing mixtures of snow and salt, at which temperature the cyanuret of chlorine is solid. Some chloride of calcium is then introduced, the stopper replaced, and the bottle kept in a moderately warm situation, in order that the moisture within may be completely absorbed. The cyanuret of chlorine is then again solidified by cold, the phial completely filled with dry and cold mercury, and a bent tube adapted to its aperture by means of a cork. The solid cyanuret of chlorine, which remains adhering to the inner surface of the phial, is converted into gas by gentle heat, and passing along the tube, is collected over mercury. Exposure to the direct solar rays interferes with the success of this process. Muriate of ammonia, together with a little carbonic acid, is then generated, and a yellow liquid collects, which appears to be a mixture of chloride of carbon and chloride of nitrogen. (An. de Ch. et Ph. xxxv. 291.)

The cyanuret of chlorine is solid at zero of Fahrenheit's thermometer, and in congealing crystallizes in very long slender needles. At temperatures between 5° F. and 10.5°, it is liquid, and also at 68° under a pressure of four atmospheres; but at the common pressure, and when the thermometer is above 10.5° or 11° F, it is a colourless gas. In the liquid state it is as limpid and colourless as water. It has a very offensive odour, irritates the eyes, is corrosive to the skin, and highly injurious to animal life.

The cyanuret of chlorine is very soluble in water and alcohol. The former under the common pressure, and at 68° F, dissolves twenty-five times its volume. Alcohol takes up 100 times its volume, and the absorption is effected almost with the same velocity as that of ammoniacal gas by water. These solutions are quite neutral with respect to litmus and turmeric paper, and may be kept without apparent change. The gas may even be separated without decomposition by boiling. The cyanuret of chlorine, accordingly, does not possess the characters of an acid.

The changes induced by the action of alkalies do not appear to be very clearly understood. M. Serullas agrees with Gay-Lussac in stating, that if to a solution of the cyanuret of chlorine a pure alkali is added, and then an acid, effervescence ensues from the escape of carbonic acid gas. Ammonia, and probably muriatic and hydrocyanic acid, is also generated.

The statement of Gay-Lussac relative to the composition of cyanuret of chlorine is confirmed by the analysis of M. Serullas. According to these chemists, it is composed of equal measures of chlorine and cyanogen gases, united without any condensation; or, by weight, of 36 parts or one equivalent of chlorine, and 26 parts or one equivalent of cyanogen. Its equivalent is therefore 62, and its specific gravity in the gaseous state, 2.1527.

## *Cyanogen and Iodine.*

The cyanuret of iodine, which was discovered in 1824 by M. Serullas, (An. de Ch. et de Ph. vol. xxvii.) may be prepared by the following process:—Two parts of the cyanuret of mercury and one of iodine, are intimately and quickly mixed in a glass mortar, and the mixture is introduced into a phial with a wide mouth. On applying heat, the violet vapours of iodine appear; but as soon as the cyanuret of mercury begins to be decomposed, the vapour of iodine is succeeded by white fumes, which, if received in a cool glass receiver, condense upon its sides into flocks like cotton wool. The action of the iodine and cyanuret of mercury is found to be promoted by the presence of a little water.

The cyanuret of iodine, when slowly condensed, occurs in very long and exceedingly slender needles, of a white colour. It has a very caustic taste and penetrating odour, and excites a flow of tears. It sinks rapidly in sulphuric acid. It is very volatile, and sustains a temperature much higher than 212° F. without decomposition; but is decomposed by a red heat. It dissolves in water and alcohol, and forms solutions which do not redden litmus paper. Alkalies act upon it in the same manner as on the cyanuret of chlorine, a compound to which it is very analogous.

Sulphurous acid, when water is present, has a very powerful action on cyanuret of iodine. On adding a few drops of this acid, iodine is set free, and hydrocyanic acid produced; but when more of the sulphurous acid is employed, the iodine disappears, and the solution is found to contain hydriodic acid. These changes are of course accompanied with the formation of sulphuric acid, and the decomposition of water.

The cyanuret of iodine has not been analyzed with accuracy; but M. Serullas infers from an approximative analysis, that it is composed of one equivalent of iodine and one of cyanogen.

## *Cyanogen and Bromine.*

The cyanuret of bromine has been prepared by M. Liebig by a process very similar to that described for procuring the cyanuret of iodine. At the bottom of a small tubulated retort, or a rather long tube, are placed two parts of cyanuret of mercury slightly moistened; and after cooling the apparatus by cold water, or still better by a freezing mixture, a precaution which is indispensable in summer, one part of bromine is introduced. Strong reaction instantly ensues, and caloric is so freely evolved, that a considerable quantity of the bromine would be dissipated, unless the temperature of the retort had been previously reduced. The new products are bromide of mercury and cyanuret of bromine, the latter of which collects in the upper part of the tube in the form of long needles. After allowing any vapour of bromine, which may have risen at the same time, to condense and fall back upon the cyanuret of mercury, the cyanuret of bromine is expelled by a gentle heat, and collected in a recipient carefully cooled.

As thus formed, the cyanuret is crystallized, sometimes in small regular colourless and transparent cubes, and sometimes in long and very slender needles. In its physical properties it is so very similar to the cyanuret of iodine, that they may easily be mistaken for each other, especially when the crystals of the cyanuret of bromine possess the acicular form. They agree closely in odour and volatility, but the

cyanuret of bromine is even more volatile than the cyanuret of iodine. It is converted into vapour at 59° F, and crystallizes suddenly on cooling. Its solubility in water and alcohol is likewise greater than that of the cyanuret of iodine. By a solution of caustic potassa it is converted into the hydrocyanate and hydrobromate of potassa.

Cyanuret of bromine is highly deleterious. A grain of it dissolved in a little water, and introduced into the œsophagus of a rabbit, proved fatal on the instant, acting with the same rapidity as prussic acid. In consequence of the volatility and noxious qualities of this substance, experiments with it should be conducted with great circumspection. The danger from this cause, together with deficient supply of bromine, prevented M. Serullas from continuing the investigation of its properties. (Edin. Journal of Science, No. xiii. 189.)

## *Ferrocyanic Acid.*

The ferrocyanic acid has, within these few years, been the subject of able researches by Mr Porrett*, Berzelius†, and M. Robiquet‡. Mr Porrett recommends two methods for obtaining ferrocyanic acid, by one of which it is procured in crystals, and by the other in a state of solution. The first process consists in dissolving 58 grains of crystallized tartaric acid in alcohol, and mixing the liquid with 50 grains of the ferrocyanate of potassa, dissolved in the smallest possible quantity of hot water. The bitartrate of potassa is precipitated, and the clear solution, on being allowed to evaporate spontaneously, gradually deposites ferrocyanic acid in the form of small cubic crystals of a yellow colour. In the second process, the ferrocyanate of baryta, dissolved in water, is mixed with a quantity of sulphuric acid, which is precisely sufficient for combining with the baryta. The insoluble sulphate of baryta subsides, and the ferrocyanic acid remains in solution. According to Mr Porrett, every ten grains of the ferrocyanate of baryta require so much liquid sulphuric acid as is equivalent to 2.53 grains of real acid.

Ferrocyanic acid is neither volatile nor poisonous in small quantities, and has no odour. It is gradually decomposed by exposure to the light, forming hydrocyanic acid and Prussian blue; but it is far less liable to spontaneous decomposition than hydrocyanic acid. It differs also from this acid in possessing the properties of acidity in a much greater degree. Thus it reddens litmus paper permanently, neutralizes alkalies, and separates the carbonic and acetic acids from their combinations. It even decomposes some salts of the more powerful acids. The peroxide of iron, for example, unites with ferrocyanic in preference to sulphuric acid, unless the latter is concentrated.

Different opinions have prevailed as to the nature of ferrocyanic acid. Berzelius maintains that it is a super-hydrocyanate of the protoxide of iron; but M. Robiquet has shown by arguments which appear to me unanswerable, that this supposition is inconsistent with the phenomena. The view which is now commonly taken of the composition of this acid, was suggested by an experiment made by Mr Porrett. On exposing ferrocyanate of soda to the agency of galvanism, the soda was observed to collect at the negative pole, while

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* Philosophical Transactions for 1814 and 1815. Annals of Philosophy, vol. xiv.

† Annales de Chimie et de Physique, vol. xv.

‡ Ibid. vol. xvii.

oxide of iron, together with the elements of hydrocyanic acid, appeared at the opposite end of the battery. From this he inferred, that the iron does not act the part of an alkali in the salt, for on that supposition it should have accompanied the soda, but that it enters into the constitution of the acid itself. Mr Porrett at first considered the iron to be in the state of an oxide; but he concludes from subsequent researches, that ferrocyanic acid contains no oxygen, and that its sole elements are carbon, hydrogen, nitrogen, and metallic iron. To the acid thus constituted, he proposes the name of *ferruretted chyazic* acid;* but the term *ferrocyanic acid* introduced by the French chemists, is more generally employed.

This view has the merit of accounting for the fact, that iron, though contained in ferrocyanic acid and all its salts, cannot be detected in them by the usual tests of iron. For the liquid tests are fitted only for detecting oxide of iron as existing in a salt, and therefore cannot be expected to indicate the presence of metallic iron, while forming one of the elements of an acid. We may now also understand how it happens that the ferrocyanic should actually contain the elements of hydrocyanic acid, and yet differ from it totally in its properties.

According to the experiments of Mr Porrett, ferrocyanic acid is composed of one equivalent of iron, one of hydrocyanic acid, and two equivalents of carbon. M. Robiquet states, however, that its elements are in such proportion as to form cyanuret of iron, and hydrocyanic acid; and the result of his researches, together with the analysis of Berzelius, appears to justify the conclusion that ferrocyanic acid is composed of

| | |
|---|---|
| Hydrogen . . . . | 2 proportionals. |
| Iron . . . . | 1 proportional. |
| Cyanogen . . . . | 3 proportionals. |

or of

| | |
|---|---|
| Hydrocyanic acid . . . | 2 proportionals. |
| Cyanuret of iron . . . | 1 proportional†. |

Ferrocyanic acid is, therefore, analogous to several acids, such as the muriatic, hydriodic, and hydrosulphuric acids, all of which contain hydrogen as an essential element, and which for this reason are termed *hydracids*. Under this point of view, ferrocyanic acid may be regarded as a compound of a certain *radical* and hydrogen. This radical, which has not been obtained in an insulated state, is composed of

| | | | | |
|---|---|---|---|---|
| Cyanogen | 3 Prop. | or of | Cyanogen | 2 Prop. |
| Iron | 1 Prop. | | Cyanuret of iron | 1 Prop. |

and the acid itself consists of one proportional of the radical and two of hydrogen.

The salts of ferrocyanic acid were once called *triple prussiates*, on the supposition that they are composed of prussic or hydrocyanic acid, in combination with oxide of iron and some other alkaline base. They are now termed *ferrocyanates*. The beautiful dye, Prussian blue, is a ferrocyanate of the peroxide of iron. It is always formed, when ferrocyanic acid or its salts are mixed in solution with a persalt of iron; and for this reason the persalts of iron, provided no free alkali is present, afford a certain and an extremely delicate test of the presence of ferrocyanic acid.

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* *Chyazic*, from the initials of carbon, hydrogen, and azote.

† See a notice on the triple prussiates in the An. de Ch. et de Ph. vol. xxii.

## *Sulphocyanic Acid.*

This acid was discovered in the year 1808 by Mr Porrett, who ascertained that it is a compound of sulphur, carbon, hydrogen, and nitrogen, and described it under the name of *sulphuretted chyazic acid*. It is now more commonly called *sulphocyanic acid*, and its salts are termed *sulphocyanates*.

Sulphocyanic acid is obtained by mixing so much sulphuric acid with a concentrated solution of the sulphocyanate of potassa as is sufficient to neutralize the alkali, and then distilling the mixture. An acid liquor collects in the recipient, which is sulphocyanic acid dissolved in water, and sulphate of potassa remains in the retort.

Sulphocyanic acid, as thus prepared, is a transparent liquid, which is either colourless or has a slight shade of pink. Its odour is somewhat similar to that of vinegar. The strongest solution of it which Mr Porrett could obtain had a specific gravity of 1.022. It boils at 216.5° F; and at 54.5° crystallizes in six-sided prisms.

Sulphocyanic acid reddens litmus paper, and forms neutral compounds with alkalies. Its presence, whether free or combined, is easily detected by a persalt of iron, with the oxide of which it unites, forming a soluble salt of a deep blood-red colour. With the protoxide of copper it yields a white salt, which is insoluble in water.

According to the analysis of Mr Porrett, (Annals of Philosophy, vol. xiii.) which is confirmed by that of Berzelius, (An. de Ch. et de Ph. vol. xvi.) sulphocyanic acid is composed of

| | | |
|---|---|---|
| Cyanogen . | 26 . | one proportional. |
| Sulphur . | 32 . | two proportionals. |
| Hydrogen . | 1 . | one proportional. |

or of

| | | |
|---|---|---|
| Bisulphuret of Cyanogen | 58 . | one proportional. |
| Hydrogen . | 1 . | one proportional. |

Sulphocyanic acid is, therefore, a hydracid; and though its radical, the bisulphuret of cyanogen, has not been obtained in a separate state, it is capable, like the radicals of all the other hydracids, of combining with metallic substances.

Berzelius also succeeded in proving the existence of a *selenio-cyanic acid*, though he could not separate it from its combination with potassa. It is likewise a hydracid, and its radical is a seleniuret of cyanogen.

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# SECTION VII.

### *COMPOUNDS OF SULPHUR.*

## *Bisulphuret of Carbon.*

This substance was discovered accidentally in the year 1796 by Professor Lampadius, who regarded it as a compound of sulphur and hydrogen, and termed it *alcohol of sulphur*. Clément and Desormes first declared it to be a sulphuret of carbon, and their statement was fully confirmed by the joint researches of Berzelius, and the late Dr Marcet. (Philos. Trans. for 1813.)

Bisulphuret of carbon may be obtained by heating in close vessels the native bisulphuret of iron (iron pyrites) with one-fifth of its weight of well-dried charcoal; or by transmitting the vapour of sulphur over fragments of charcoal heated to redness in a tube of porcelain. The compound, as it is formed, should be conducted by means of a glass tube into cold water, at the bottom of which it is collected. To free it from moisture and adhering sulphur, it should be distilled at a low temperature in contact with the chloride of calcium.

Bisulphuret of carbon is a transparent colourless liquid, which is remarkable for its high refractive power. Its specific gravity is 1.272. It has an acid, pungent, and somewhat aromatic taste, and a very fetid odour. It is exceedingly volatile;—its vapour at 63.5° F. supports a column of mercury 7.36 inches long; and at 110° F. it enters into brisk ebullition. From its great volatility it may be employed for producing an intense degree of cold.

Bisulphuret of carbon is very inflammable, and kindles in the open air at a temperature scarcely exceeding that at which mercury boils. It burns with a pale blue flame. Admitted into a vessel of oxygen gas, so much vapour rises as to form an explosive mixture; and when mixed in like manner with deutoxide of nitrogen, it forms a combustible mixture, which is kindled on the approach of a lighted taper, and burns rapidly, with a large greenish-white flame of dazzling brilliancy. It dissolves readily in alcohol and ether, and is precipitated from the solution by water. It dissolves sulphur, phosphorus, and iodine, and the solution of the latter has a beautiful pink colour. Chlorine decomposes it, with formation of the chloride of sulphur. The pure acids have little action upon it. With the alkalies it unites slowly, forming compounds which Berzelius calls *carbo-sulphurets*. It is converted by strong nitro-muriatic acid into a white crystalline substance like camphor, which Berzelius considers to be a compound of muriatic, carbonic, and sulphurous acid gases.

*Xanthogen and Hydroxanthic acid.*—M. Zeise, Professor of chemistry in Copenhagen, has discovered some novel and interesting facts, relative to the bisulphuret of carbon. When this fluid is agitated with a solution of pure potassa in strong alcohol, the alkaline properties of the potassa disappear entirely; and on exposing the solution to a temperature of 32° F. numerous acicular crystals are deposited. M. Zeise attributes these phenomena to the formation of a new acid, the elements of which are derived, in his opinion, partly from the alcohol, and partly from the bisulphuret of carbon. He regards the acid as a compound of carbon, sulphur, and hydrogen. He supposes it to be a hydracid, and that its radical is a sulphuret of carbon. To the radical of this hydracid he applies the term *Xanthogen*, (from ξανθος *yellow*, and γεννάω *I generate*,) expressive of the fact that its combinations with several metals have a yellow colour. The acid itself is called *hydroxanthic acid*, and its salts *hydroxanthates*. The crystals deposited from the alcoholic solution are the hydroxanthate of potassa.

There is no doubt of a new acid being generated under the ircumstances described by M. Zeise; but since he has not procured xanthogen in an insulated form, nor even determined with certainty the constituent principles of the hydroxanthic acid, there exists considerable uncertainty as to its real nature. On this account I refer to the original essay for more ample details concerning it. (An de Ch. et de Ph. vol. xxi; and Annals of Philosophy, N. S. vol. iv.)

*Sulphuret of Phosphorus.*—When sulphur is brought into contact with fused phosphorus, they unite readily, but in proportions which have not been precisely determined; and they frequently react on

each other with such violence as to cause an explosion. For this reason the experiment should be made with a quantity of phosphorus not exceeding thirty or forty grains. The phosphorus is placed in a glass tube, five or six inches long, and about half an inch wide, and when by a gentle heat it is liquefied, the sulphur is added to it in successive small portions. Caloric is evolved at the moment of combination, and sulphuretted hydrogen and phosphoric acid, owing to the presence of moisture, are generated. This compound may also be made by agitating the flowers of sulphur with fused phosphorus under water. The temperature should not exceed 160° F; for otherwise sulphuretted hydrogen and phosphoric acid would be evolved so freely as to prove dangerous, or at least to interfere with the success of the process.

The sulphuret of phosphorus, from the nature of its elements, is highly combustible. It is much more fusible than phosphorus. A compound made by Mr Faraday with about five parts of sulphur to seven of phosphorus, was quite fluid at 32° F, and did not solidify at 20° F. (Quarterly Journal, vol. iv.)

## SECTION VIII.

### *COMPOUNDS OF SELENIUM.*

### *Sulphuret of Selenium.*

When sulphuretted hydrogen gas is conducted into a solution of selenic acid, an orange-coloured precipitate subsides, which is a sulphuret of selenium. It fuses at a heat a little above 212° F, and at a still higher temperature may be sublimed without change. In the open air it takes fire when heated, and sulphurous, selenious, and selenic acids are the products of its combustion. The alkalies and alkaline hydrosulphurets dissolve it. Nitric acid acts upon it with difficulty; but nitro-muriatic acid converts it into sulphuric and selenic acids. (Annals of Philosophy, vol. xiv.) According to Berzelius, this sulphuret is composed of 40 parts or one proportional of selenium, and 24 parts or one proportional and a half of sulphur.

Selenium and sulphur combine readily by the aid of heat, but it is difficult in this way to obtain a definite compound.

### *Phosphuret of Selenium.*

The phosphuret of selenium may be prepared in the same manner as the sulphuret of phosphorus; but as selenium is capable of uniting with phosphorus in several proportions, the compound formed by fusing them together can hardly be supposed to be of a definite nature. This phosphuret is very fusible, sublimes without change in close vessels, and is inflammable. It decomposes water gradually when digested in it, giving rise to seleniuretted hydrogen, and one of the acids of phosphorus. (Annals of Philosophy, vol. xiv.)

# METALS.

## GENERAL PROPERTIES OF METALS.

Metals are distinguished from other substances by the following properties. They are all conductors of electricity and caloric. When combined with oxygen, chlorine, iodine, sulphur, or similar substances, and the resulting compounds are submitted to the action of galvanism, the metals always appear at the negative side of the battery, and for this reason are said to be positive electrics. They are quite opake, refusing a passage to light, though reduced to very thin leaves. They are in general good reflectors of light, and possess a peculiar lustre, which is termed the metallic lustre. Every substance in which these characters reside may be regarded as a metal.

The number of metals, the existence of which is admitted by chemists, amounts to forty. The following table contains the names of those that have been procured in a state of purity, together with the date at which they were discovered, and the names of the chemists by whom the discovery was made.

*Table of the Discovery of Metals.*

| *Names of Metals.* | *Authors of the Discovery.* | *Dates of the Discovery.* |
|---|---|---|
| Gold | Known to the Ancients. | |
| Silver | Known to the Ancients. | |
| Iron | Known to the Ancients. | |
| Copper | Known to the Ancients. | |
| Mercury | Known to the Ancients. | |
| Lead | Known to the Ancients. | |
| Tin | Known to the Ancients. | |
| Antimony | Described by Basil Valentine, | 15th century. |
| Zinc | Described by Agricola in | 1520 |
| Bismuth | First mentioned by Paracelsus, | 16th century. |
| Arsenic | Brandt, in | 1733 |
| Cobalt | Brandt, in | 1733 |
| Platinum | Wood, Assay Master, Jamaica, | 1741 |
| Nickel | Cronstedt, | 1751 |
| Manganese | Gahn and Scheele, | 1774 |
| Tungsten | MM. D'Elhuyart, | 1781 |
| Tellurium | Müller, | 1782 |
| Molybdenum | Hielm, | 1782 |
| Uranium | Klaproth, | 1789 |
| Titanium | Gregor, | 1791 |
| Chromium | Vauquelin | 1797 |
| Columbium | Hatchett, | 1802 |

| *Names of Metals.* | *Authors of the Discovery.* | *Dates of the Discovery.* |
|---|---|---|
| Palladium<br>Rhodium | Dr Wollaston, | 1803 |
| Iridium | Descotils and Smithson Tennant, | 1803 |
| Osmium | Smithson Tennant, | 1803 |
| Cerium | Hisinger and Berzelius, | 1804 |
| Potassium<br>Sodium<br>Barium<br>Strontium<br>Calcium | Sir H. Davy, | 1807 |
| Cadmium | Stromeyer, | 1818 |
| Lithium | Arfwedson, | 1818 |
| Silicium<br>Zirconium | Berzelius, | 1824 |

Most of the metals are remarkable for their great specific gravity; some of them, such as gold and platinum, which are the densest known bodies in nature, being more than nineteen times heavier than an equal bulk of water. Great specific gravity was once supposed to be an essential character of metals; but the discovery of potassium and sodium, which are so light as to float on the surface of water, has shown that this supposition is erroneous. Some metals experience an increase of density to a certain extent when hammered, their particles being permanently approximated by the operation. On this account the specific gravity of some of the metals contained in the following table, is represented as varying between two extremes:—

*Table of the Specific Gravity of Metals at 60° Fahr. compared to Water as unity.*

| | | |
|---|---|---|
| Platinum | 20.98 | Brisson. |
| Gold | 19.257 | Do. |
| Tungsten | 17.6 | D'Elhuyart. |
| Mercury | 13.568 | Brisson. |
| Palladium | 11.3 to 11.8 | Wollaston. |
| Lead | 11.352 | Brisson. |
| Silver | 10.474 | Do. |
| Bismuth | 9.822 | Do. |
| Uranium | 9.000 | Bucholz. |
| Copper | 8.895 | Hatchett. |
| Cadmium | 8.604 | Stromeyer. |
| Cobalt | 8.538 | Haüy. |
| Arsenic | 8.308 | Bergmann. |
| Nickel | 8.279 | Richter. |
| Iron | 7.788 | Brisson. |
| Molybdenum | 7.400 | Hielm. |
| Tin | 7.291 | Brisson. |
| Zinc | 6.861 to 7.1 | Do. |
| Manganese | 6.850 | Bergmann. |
| Antimony | 6.702 | Brisson. |
| Tellurium | 6.115 | Klaproth. |
| Titanium | 5.3 | Wollaston. |
| Cerium | 4.489 to 4.619 | Hisinger and Berzelius. |
| Sodium | 0.972 | Gay-Lussac and Thenard. |
| Potassium | 0.865 | |

X

Some metals possess the property of *malleability*, that is, admit of being beaten into thin plates or leaves by hammering. The malleable metals are gold, silver, copper, tin, platinum, palladium, cadmium, lead, zinc, iron, nickel, potassium, sodium, and frozen mercury. The other metals are either malleable in a very small degree only, or, like antimony, arsenic, and bismuth, are actually brittle. Gold surpasses all metals in malleability:—one grain of it may be extended so as to cover about 52 square inches of surface, and to have a thickness not exceeding 1-282020th of an inch.

Nearly all malleable metals may be drawn out into wires, a property which is expressed by the term *ductility*. The only metals which are remarkable in this respect are gold, silver, platinum, iron, and copper. Dr Wollaston has described a method by which gold wire may be obtained so fine that its diameter shall be only 1-5000th of an inch, and that 550 feet of it are required to weigh one grain. He has obtained a platinum wire so small, that its diameter did not exceed 1-30,000th of an inch. (Philos. Transactions for 1818.) It is singular that the ductility and malleability of the same metal are not always in proportion to one another. Iron, for example, cannot be made into fine leaves, but it may be drawn into very small wires.

The tenacity of metals is measured by ascertaining the greatest weight which a wire of a certain thickness can support, without breaking. According to the experiments of Guyton-Morveau, whose results are comprised in the following table, iron, in point of tenacity, surpasses all other metals.

The diameter of each wire was 0.787th of a line.

| | *Pounds.* |
|---|---|
| Iron wire supports . . . . . | 549.25 |
| Copper . . . . . . | 302.278 |
| Platinum . . . . . . | 274.32 |
| Silver . . . . . . . | 187.137 |
| Gold . . . . . . . | 150.753 |
| Zinc . . . . . . . | 109.54 |
| Tin . . . . . . . | 34.63 |
| Lead . . . . . . . | 27.621 |

The metals differ also in hardness, but I am not aware that their exact relation to one another, under this point of view, has been determined by experiment. In the list of hard metals may be placed titanium, manganese, iron, nickel, copper, zinc, and palladium. Gold, silver, and platinum are softer than these; lead is softer still, and potassium and sodium yield to the pressure of the fingers. The properties of elasticity and sonorousness are allied to that of hardness. Iron and copper are in these respects the most conspicuous.

Many of the metals have a distinctly crystalline texture. Iron, for example, is fibrous; and zinc, bismuth, and antimony, are lamellated. Metals are sometimes obtained also in crystals; and when they do crystallize, they always assume the figure of a cube, the regular octahedron, or some form allied to it. Gold, silver, and copper occur naturally in crystals, while others crystallize when they pass gradually from the liquid to the solid condition. Crystals are most readily procured from those metals which fuse at a low temperature; and bismuth, from conducting caloric less perfectly than other metals, and therefore cooling more slowly, is best fitted for the purpose. The process should be conducted in the way already described for forming crystals of sulphur. (Page 177.)

The metals, with the exception of mercury, are solid at common

temperatures; but they may all be liquefied by heat. The degree at which they *fuse*, or their *point* of *fusion*, is very different for different metals, as will appear by inspecting the following table. (Thenard's Chemistry, vol. i.)

*Table of the fusibility of different Metals.*

| | Metal | Temperature | Authority |
|---|---|---|---|
| | | *Fahr.* | |
| *Fusible below a red heat.* | Mercury | —39° | Different Chemists. |
| | Potassium | 136 | Gay-Lussac and Thenard. |
| | Sodium | 190 | Gay-Lussac and Thenard. |
| | Tin | 430 | Newton. |
| | Bismuth | 498 | Newton. |
| | Lead | 500 | Biot. |
| | Tellurium—rather less fusible than lead | | Klaproth. |
| | Arsenic—undetermined. | | |
| | Zinc | 698 | Brongniart. |
| | Antimony—a little below a red heat. | | |
| | Cadmium | | Stromeyer. |
| | | *Pyrometer of Wedgwood.* | |
| *Infusible below a red heat.* | Silver | 20° | Kennedy |
| | Copper | 27 | Wedgwood. |
| | Gold | 32 | Wedgwood. |
| | Cobalt—rather less fusible than iron. | | |
| | Iron | 130 | Wedgwood. |
| | | 158 | Mackenzie. |
| | Manganese | 160 | Guyton. |
| | Nickel—the same as Manganese | | Richter. |
| | Palladium. | | |
| | Molybdenum, Uranium, Tungsten, Chromium | Almost infusible, and not to be procured in buttons by the heat of a smith's forge. | Fusible before the oxy-hydrogen blowpipe. |
| | Titanium, Cerium, Osmium, Iridium, Rhodium, Platinum, Columbium | Infusible in the heat of a smith's forge, but fusible before the oxy-hydrogen blowpipe. | |

The metals differ also in volatility. Some are readily volatilized by caloric, while others are of so fixed a nature that they may be exposed to the most intense heat of a wind furnace without being dissipated in vapour. There are seven metals, the volatility of which has been ascertained with certainty; namely, cadmium, mercury, arsenic, tellurium, potassium, sodium, and zinc.

The metals cannot be resolved into more simple parts, and, therefore, in the present state of chemistry, they must be regarded as elementary bodies. It was formerly conceived that they might be converted into one another; and this notion led to the vain attempts of the alchemists to convert the baser metals into gold. The chemist has now learned that his sole art consists in resolving compound bodies into their elements, and causing substances to unite which were

previously uncombined. There is not a single fact in support of the opinion that one elementary principle can assume the properties peculiar to another.

Metals have an extensive range of affinity, and on this account few of them are found in the earth *native*, that is, in an uncombined form. They commonly occur in combination with other bodies, especially with oxygen and sulphur, in which state they are said to be *mineralized*. It is a singular fact in the chemical history of the metals, that they are little disposed to combine in the metallic state with compound bodies. Chemists are not acquainted with any instance of a metal forming a definite compound either with a metallic oxide or with an acid. They unite readily, on the contrary, with elementary substances. Thus, under favourable circumstances, they combine with one another, yielding compounds termed *alloys*, which possess all the characteristic physical properties of the pure metals. They unite likewise with the simple substances not metallic, such as oxygen, chlorine, and sulphur, giving rise to new bodies in which the metallic character is wholly wanting. In all these combinations the same tendency to unite in a few definite proportions is conspicuous, as in that department of the science of which I have just completed the description. The chemical changes are regulated by the same general laws; and in describing them, the same nomenclature is applicable.

The method which I propose to adopt in treating the metallic bodies has already been explained in the introduction. Before proceeding, however, to describe the metals individually, I shall make some general observations by which the study of this subject will be much facilitated.

Metals are of a combustible nature, that is, they are not only susceptible of slow oxidation, but, under favourable circumstances, they unite rapidly with oxygen, giving rise to all the phenomena of real combustion. Zinc burns with a brilliant flame when heated to full redness in the open air; iron emits vivid scintillations on being inflamed in an atmosphere of oxygen gas; and the least oxidable metals, such as gold and platinum, scintillate in a similar manner when heated by the oxy-hydrogen blowpipe.

The product either of the slow or rapid oxidation of a metal, when heated in the air, has an earthy aspect, and was called a *calx* by the older chemists, the process of forming it being expressed by the term *calcination*. Another method of oxidizing metals is by *deflagration;* that is, by mixing them with the nitrate or chlorate of potassa, and projecting the mixture into a red-hot crucible. Most metals may be oxidized by digestion in nitric acid; and nitro-muriatic acid is an oxidizing agent of still greater power.

Some metals unite with oxygen in one proportion only, but most of them have two or three degrees of oxidation. Metals differ remarkably in their relative forces of attraction for oxygen. Potassium and sodium, for example, are oxidized by mere exposure to the air; and they decompose water at all temperatures, the instant they come in contact with it. Iron and copper may be preserved in dry air without change, nor can they decompose water at common temperatures; but they are both slowly oxidized by exposure to a moist atmosphere, and combine rapidly with oxygen when heated to redness in the open air. Iron has a stronger affinity for oxygen than copper; for the former decomposes water at a red heat, whereas the latter cannot produce that effect. Mercury is less inclined than copper to unite with oxygen. Thus it may be exposed without change to the influence of a moist atmosphere. At a temperature of 650° or 700° F. it is oxidized; but

at a red heat it is reduced to the metallic state, while the oxide of copper can sustain the strongest heat of a blast furnace without losing its oxygen. The affinity of silver for oxygen is still weaker than that of mercury; for it cannot be oxidized by the sole agency of caloric at any temperature.

Metallic oxides suffer *reduction*, or may be *reduced* to the metallic state, in several ways:

1. By heat alone. By this method the oxides of gold, silver, mercury, and platinum, may be decomposed.

2. By the united agency of heat and combustible matter. Thus, by transmitting a current of hydrogen gas over the oxides of copper or iron, heated to redness in a tube of porcelain, water is generated, and the metals are obtained in a pure form. Carbonaceous matters are likewise used for the purpose with great success. Potassa and soda, for example, may be decomposed by exposing them to a white heat after being intimately mixed with charcoal in fine powder. A similar process is employed in metallurgy for procuring the metals from their ores, the inflammable materials being wood, charcoal, coke, or coal. In the more delicate operations of the laboratory, charcoal and the *black flux* are preferred.

3. By the galvanic battery. This is a still more powerful agent than the preceding; since some oxides, such as baryta and strontia, which resist the united influence of heat and charcoal, are reduced by the agency of galvanism.

4. By the action of deoxidizing agents on metallic solutions. The phosphorous acid, for example, when added to a liquid containing the oxide of mercury, deprives the oxide of its oxygen, metallic mercury subsides, and phosphoric acid is generated. In like manner, one metal may be precipitated by another, provided the affinity of the latter for oxygen exceeds that of the former. Thus, when mercury is added to a solution of the nitrate of the oxide of silver, metallic silver is thrown down, and oxide of mercury is dissolved by the nitric acid. On placing metallic copper in the liquid, pure mercury subsides, and a nitrate of the oxide of copper is formed; and from this solution metallic copper may be precipitated by means of iron.

Metals, like the simple non-metallic bodies, may give rise to oxides or acids by combining with oxygen. The former are the most frequent products. Many metals which are not acidified by oxygen may be formed into oxides; whereas one metal only, arsenic, is capable of forming an acid and not an oxide. All the other metals which are convertible into acids by oxygen, such as chromium, tungsten, and molybdenum, are also susceptible of yielding one or more oxides. In these instances, the acids always contain a larger quantity of oxygen than the oxides of the same metal.

The distinguishing feature of the metallic oxides is the property which many possess of entering into combination with acids. All salts, those of ammonia excepted, are composed of an acid and a metallic oxide. In some instances all the oxides of the same metal are capable of forming salts with acids, as is exemplified by the oxides of iron. More commonly, however, the protoxide is the sole *alkaline* or *salifiable base*. Most of the metallic oxides are insoluble in water; but all those that are soluble have the property of giving a brown stain to yellow turmeric paper, and of restoring the blue colour of reddened litmus.

Oxides sometimes unite with each other, and form definite compounds. The most abundant ore of chromium, commonly called chromate of iron, is an instance of this kind; and the red and deutox-

ide of manganese, and the red oxide of lead, appear to belong to the same class of bodies.

Chlorine has a powerful affinity for metallic substances. It combines readily with most metals at common temperatures, and the action is in many instances so violent as to be accompanied with the evolution of light. For example, when powdered zinc, arsenic, or antimony, is thrown into a jar of chlorine gas, the metal is instantly inflamed. The attraction of chlorine for metals even surpasses that of oxygen. Thus, when chlorine is brought into contact at a red heat with pure lime, magnesia, baryta, strontia, potassa, or soda, oxygen is emitted, and a chloride of the metal is generated, the elements of which are so strongly united, that no temperature hitherto tried can separate them. All other metallic oxides are, with few exceptions, acted on in the same manner by chlorine, and in some cases the change takes place below the temperature of ignition.

All the metallic chlorides are solid at the common temperature, except the bichlorides of tin and arsenic, which are liquid. They are fusible by heat, assume a crystalline texture in cooling, and under favourable circumstances crystallize with regularity. Several of them, such as the chlorides of tin, arsenic, antimony, and mercury, are volatile, and may be sublimed without change. They are for the most part colourless, do not possess the metallic lustre, and have the aspect of a salt. Two of the chlorides are insoluble in water, namely, the chloride of silver and protochloride of mercury; but all the others are more or less soluble in water.

Two only of the metallic chlorides, those namely of gold and platinum, are decomposable by heat. All the chlorides of the common metals are decomposed at a red heat by hydrogen gas, muriatic acid being disengaged while the metal is set free. Pure charcoal does not effect their decomposition; but if moisture be present at the same time, muriatic and carbonic acid gases are formed, and the metal remains. They resist the action of anhydrous sulphuric acid; but all the chlorides, excepting those of silver and mercury, are readily decomposed by hydrated sulphuric acid, with disengagement of muriatic acid gas. The change is accompanied with the decomposition of water, the hydrogen of which combines with chlorine, and its oxygen with the metal. All chlorides, when in solution, may be recognised by yielding with nitrate of silver a white precipitate, which is chloride of silver.

Metallic chlorides may in most cases be formed by direct action of chlorine on the pure metals. They are also frequently procured by evaporating a solution of the muriate of a metallic oxide to dryness, and applying heat so long as any water is expelled. Metallic chlorides are often deposited from such solutions by crystallization.

Chlorine manifests a feeble affinity for metallic oxides. No combination of the kind occurs at a red heat, and no chloride of a metallic oxide can be heated to redness without decomposition. Such compounds can only be formed at low temperatures; and they are possessed of little permanency. It is well known that chlorine may combine under favourable circumstances with the alkalies and alkaline earths; and M. Grouvelle has succeeded in making it unite with magnesia, and the oxides of zinc, copper, and iron. (An. de Ch. et de Ph. vol. xvii.) Of these chlorides, that of potassa may be taken as an example. If chlorine is conducted into a dilute and cold solution of pure potassa, the chloride of that alkali will be produced; but the affinity which gives rise to its formation is not sufficient for rendering

it permanent. It is destroyed by most substances that act on either of its constituents. The addition of an acid produces this effect by combining with the alkali, and hence the chlorine is separated by the carbonic acid of the atmosphere. Animal or vegetable colouring matters are fatal to the compound by giving chlorine an opportunity to exert its bleaching power; and, indeed, the colour is removed by the chloride of potassa almost as readily as by a solution of chlorine in pure water. It is also destroyed by the action of heat; nor can its solution be concentrated without decomposition; for, in either case, muriatic and chloric acids are generated. (Page 197.)

Iodine has a strong attraction for metals; the most of the compounds which it forms with them sustain a red heat in close vessels without decomposition. But in the degree of its affinity for metallic substances, it is inferior to chlorine and oxygen. We have seen that chlorine has a stronger affinity than oxygen for metals, since it decomposes nearly all oxides at high temperatures; and it separates iodine also from metals under the same circumstances. If the vapour of iodine is brought into contact with potassa, soda, protoxide of lead, or the oxide of bismuth, heated to redness, oxygen gas is evolved, and an iodide of these metals will be formed. But iodine, so far as is known, cannot separate oxygen from any other metal; nay, all the iodides, except those just mentioned, are decomposed by exposure to oxygen gas at the temperature of ignition. All the iodides are decomposed by chlorine, bromine, and concentrated sulphuric and nitric acids; and the iodine which is set free may be recognised either by the colour of its vapour, or by its action on starch. (Page 212.) The metallic iodides are generated under circumstances analogous to those above mentioned for procuring the chlorides.

When the vapour of iodine is conducted over red-hot lime, baryta, or strontia, oxygen is not disengaged, but an iodide of those oxides, according to Gay-Lussac, is generated. The iodides of these oxides are, therefore, more permanent than the analogous compounds with chlorine. Iodine does not combine with any other oxide under the same circumstances; and indeed all other such iodides, very few of which exist, are, like the chlorides of oxides, possessed of little permanency, and are decomposed by a red heat.

The action of iodine on metallic oxides, when dissolved or suspended in water, is precisely analogous to that of chlorine. On adding iodine to a solution of the pure alkalies or alkaline earths, water is decomposed, and hydriodic and iodic acids are generated.

Bromine, in its affinity for metallic substances, is intermediate between chlorine and iodine; for while chlorine disengages bromine from its combination with metals, the metallic iodides are decomposed by bromine. The same phenomena attend the union of bromine with metals, as accompanies the formation of metallic chlorides. Thus antimony and tin takes fire by contact with bromine, and its action with potassium is attended with a flash of light and intense disengagement of caloric. These compounds have as yet been but partially examined. They may be formed either by the action of bromine on the pure metals, or by dissolving metallic oxides in hydrobromic acid, and evaporating the solution to dryness.

As fluorine has not hitherto been obtained in a separate state, the nature of its action on the metals is unknown; but the chief difficulty of procuring it in an insulated form appears to arise from its extremely

powerful affinity for metallic substances, in consequence of which, at the moment of becoming free, it attacks the vessels and instruments employed in its preparation. The best mode of preparing the soluble fluorides, such as those of potassium and sodium, is by dissolving the carbonate of potassa or soda in hydrofluoric acid, and evaporating the solution to perfect dryness. The insoluble fluorides are easily formed from the hydrofluates of potassa and soda by double decomposition. These compounds are without exception decomposed by concentrated sulphuric acid with the aid of heat; and the hydrofluoric acid, in escaping, may easily be detected by its action on glass.

Sulphur, like the preceding elementary substances, has a strong tendency to unite with metals, and the combination may be effected in several ways:—

1. By heating the metal directly with sulphur. The metal, in the form of powder or filings, is mixed with a due proportion of sulphur and the mixture heated in an earthen crucible, which is covered to prevent the access of air. Or if the metal can sustain a red heat without fusing, the vapour of sulphur may be passed over it while heated to redness in a tube of porcelain. The act of combination, which frequently ensues below the temperature of ignition, is attended by free disengagement of caloric; and in several instances the heat evolved is so great, that the whole mass becomes luminous and shines with a vivid light. This appearance of combustion, which occurs quite independently of the presence of oxygen, is exemplified by the sulphurets of potassium, sodium, copper, iron, lead, and bismuth.

2. By igniting a mixture of a metallic oxide and sulphur. The sulphurets of the common metals may be made by this process. The elements of the oxide unite with separate portions of sulphur, forming sulphurous acid gas, which is disengaged, and a metallic sulphuret which remains in the retort.

3. By depriving the sulphate of an oxide of its oxygen by means of heat and combustible matter. Charcoal or hydrogen gas may be employed for the purpose, as will be described immediately.

4. By sulphuretted hydrogen, or an alkaline hydrosulphuret. Nearly all the salts of the common metals are decomposed, when a current of sulphuretted hydrogen gas is conducted into their solutions. The salts of uranium, iron, manganese, cobalt, and nickel, are well-known exceptions; but these also are precipitated by the hydrosulphuret of ammonia or potassa.

The sulphurets are opake brittle solids, many of which, such as the sulphurets of lead, antimony, and iron, have a metallic lustre. They are all fusible by heat, and commonly assume a crystalline texture in cooling. Most of them are fixed in the fire; but the sulphurets of mercury and arsenic are remarkable for their volatility. All the sulphurets, excepting those which are formed of the metallic bases of the alkalies and earths, are insoluble in water.

Most of the protosulphurets are capable of supporting intense heat without decomposition; but those which contain more than one equivalent of sulphur, lose part of it when strongly heated. They are all decomposed without exception by exposure to the combined agency of heat and air or oxygen gas; and the products depend entirely on the degree of heat and the nature of the metal. The sulphuret is converted into the sulphate of an oxide, provided the sulphate is able to support the temperature employed in the operation. If this is not the case, then the sulphur is evolved under the form of sulphurous

acid, and a metallic oxide is left; or if the oxide itself is decomposed by heat, the pure metal remains. The action of heat and air in decomposing metallic sulphurets is the basis of several metallurgic processes. A few sulphurets are decomposed by the action of hydrogen gas at a red heat, the pure metal being set free and sulphuretted hydrogen evolved. M. Rose finds that the only sulphurets which admit of being easily reduced to the metallic state in this way are those of antimony, bismuth, and silver. The sulphuret of tin is decomposed with difficulty, and requires a very high temperature. All the other sulphurets which he subjected to this treatment, were either deprived of a part only of their sulphur, such as the bisulphuret of iron, or were nor attacked at all, as happened with the sulphurets of zinc, lead, and copper. (Poggendorff's Annalen, iv. 109.)

Many of the metallic sulphurets were formerly thought to be compounds of sulphur and a metallic oxide; and I believe this was first shown to be an error by Proust in the essays which he published in the *Journal de Physique*. In the 53d volume of that work, he demonstrated that the sulphuret of iron, (magnetic pyrites), as well as the common cubic pyrites or bisulphuret, are compounds of sulphur and metallic iron without any oxygen. He showed the same also with respect to the sulphurets of other metals, such as those of mercury and copper. He was of opinion, however, that in some instances sulphur does unite with a metallic oxide. Thus, when sulphur and the peroxide of tin are heated together, sulphurous acid is disengaged, and the residue according to Proust is a sulphuret of the protoxide.

It was the general belief at that time, also, that the compounds formed by heating sulphur with an alkali or alkaline earth are sulphurets of a metallic oxide. Thus, the old *hepar sulphuris*, the *sulphuretum potassæ* of the Edinburgh Pharmacopœia, which is made by fusing together a mixture of sulphur and dry carbonate of potassa, was regarded as a sulphuret of potassa. In the year 1817 M. Vauquelin published an essay in the 6th volume of the *Annales de Chimie et de Physique*, wherein he detailed some experiments, the object of which was to determine the state of the alkali in that compound. The late Count Berthollet had observed that when *hepar sulphuris* is dissolved in water, the solution always contains a considerable portion of sulphuric acid, which he conceived to be generated at the moment of solution. He supposed that water is then decomposed; and that its elements combine with different portions of sulphur, the oxygen giving rise to the formation of sulphuric acid, and the hydrogen to sulphuretted hydrogen. The accuracy of this explanation was called in question by Vauquelin in the paper above mentioned, who contended that the sulphuric acid is generated, not during the process of solution, but by the action of heat during the formation of the sulphuret. One portion of potassa, according to him, yields its oxygen at a high temperature to some of the sulphur, converting it into sulphuric acid, while the potassium unites with pure sulphur. Two combinations therefore result—sulphuret of potassium and sulphate of potassa, which are mixed together. Though the experiments adduced in favour of this opinion were not absolutely convincing, yet they made it the more probable of the two; and M. Vauquelin, admitting however the want of actual proof, inferred from them that when an alkaline oxide is heated to redness with sulphur, the former loses oxygen, and a sulphuret of the metal itself is produced.

The sixth volume of the Annals likewise contains a paper by M.

Gay-Lussac, who offered additional arguments in favour of Vauquelin's opinion, and I believe most chemists held them to be satisfactory. But the more recent labours of MM. Berthier and Berzelius have given still greater insight into the nature of these compounds. One of Vauquelin's chief arguments was drawn from the action of charcoal on sulphate of potassa. When a mixture of this salt with powdered charcoal is ignited without exposure to the air, carbonic oxide and carbonic acid gases are formed, and a sulphuret is left, analogous both in appearance and properties to that which may be made by igniting carbonate of potassa directly with sulphur. They are both essentially the same substance, and Vauquelin conceived from the strong attraction of carbon for oxygen, that both the sulphuric acid and potassa would be decomposed by charcoal at a high temperature; and that, consequently, the product must be a sulphuret of potassium.

M. Berthier has proved in the following manner that these changes do actually occur. (An. de Ch. et de Ph. vol. xxii.) He put a known weight of sulphate of baryta into a crucible lined with a mixture of clay and charcoal, defended it from contact with the air, and exposed it to a white heat for the space of two hours. By this treatment it suffered complete decomposition, and it was found that in passing into a sulphuret, it had suffered a loss in weight precisely equal to the quantity of oxygen originally contained in the acid and earth. This circumstance, coupled with the fact that there had been no loss of sulphur, is decisive evidence that the baryta as well as the acid had lost its oxygen, and that a sulphuret of barium had been formed. He obtained the same results also with the sulphates of strontia, lime, potassa, and soda; but from the fusibility of the sulphurets of potassium and sodium, their loss of weight could not be determined with such precision as in the other instances.

The experiments of Berzelius, performed about the same time, are exceedingly elegant, and still more satisfactory than the foregoing. (An de Ch. et de Ph. vol. xx.) He transmitted a current of dry hydrogen gas over a known quantity of sulphate of potassa, heated to redness. It was expected from the strong affinity of hydrogen for oxygen, that the sulphate would be decomposed; and, accordingly, a considerable quantity of water was formed, which was carefully collected and weighed. The loss of weight which the salt had experienced, was precisely equivalent to the oxygen of the acid and alkali; and the oxygen of the water was exactly equal to the loss in weight. A similar result was obtained with the sulphates of soda, baryta, strontia, and lime.

It is demonstrated, therefore, that the metallic bases of the alkalies and alkaline earths agree with the common metals in their disposition to unite with sulphur. It is now certain that, whether a sulphate be decomposed by hydrogen or charcoal, or sulphur ignited with an alkali or an alkaline earth, a metallic sulphuret is always the product. Direct combination between sulphur and a metallic oxide is a rare occurrence, and I am not aware that the existence of such a compound has as yet been clearly established. Gay-Lussac indeed states that, when an alkali or an alkaline earth is heated with sulphur in such a manner that the temperature is never so high as a low red heat, the product is really the sulphuret of an oxide. But the facts adduced in favour of this opinion are not altogether satisfactory, so that the real nature of the product must be decided by future observation.

Several of the metallic sulphurets occur abundantly in nature,

Those that are most frequently met with, are the sulphurets of lead, antimony, copper, iron, zinc, molybdenum, and silver.

The metallic seleniurets have so close a resemblance in their chemical relations to the sulphurets, that it is unnecessary to give a separate description of them. They may be prepared either by bringing selenium in contact with the metals at a high temperature, or by the action of hydro-selenic acid on metallic solutions.

Cyanogen, as already mentioned at page 251, has an affinity for metallic substances. Few of the cyanurets, however, have been hitherto obtained in a separate state, excepting those of potassium, mercury, silver, and palladium. The three latter are readily decomposed by a red heat.

Cyanogen unites also with some of the metallic oxides. When hydrocyanic acid vapour is transmitted over pure baryta contained in a porcelain tube, and heated till it begins to be luminous, hydrogen gas is evolved, and cyanuret of baryta, according to Gay-Lussac, is generated. The same chemist succeeded in forming the cyanurets of potassa and soda by a similar process. These compounds exist only in the dry state. A change is produced in them by the action of water, the nature of which has already been explained. (Page 254.)

Respecting the preceding compounds there remains one subject, the consideration of which, as applying equally to all, has been purposely delayed. The non-metallic ingredient of each of these compounds is the radical of a hydracid; that is, it has the property of forming with hydrogen an acid, which, like other acids, is unable to unite with metals, but appears to combine readily with many metallic oxides. Owing to this circumstance, a difficulty arises in explaining the action of such substances on water. Thus, when the chloride of potassium is put into water, it may dissolve without suffering any other chemical change, and the liquid accordingly contain chloride of potassium in solution. But it is also possible that the elements of this compound may react on those of water, its potassium uniting with oxygen, and its chlorine with hydrogen; and as the resulting potassa and muriatic acid have a strong affinity for each other, the solution would of course contain muriate of potassa. A similar uncertainty attends the action of water on other metallic chlorides, and on the compounds of metals with iodine, bromine, sulphur, and similar substances; so that when the iodide, sulphuret, and cyanuret of potassium are put into water, chemists are in doubt whether they are dissolved as such, or whether they may not be converted, by decomposition of water, into the hydriodate, hydrosulphate, and hydrocyanate of potassa. This question would at once be decided, could it be ascertained whether water is or is not decomposed during the process of solution; but this is the precise point of difficulty, since, from the operation of the laws of chemical union, no disengagement of gas does or can take place by which the occurrence of such a change may be indicated. Chemists, accordingly, being guided by probabilities, are divided in opinion, and I shall, therefore, give a brief statement of both views, with the arguments in favour of each.

According to one view, then, the chloride of potassium and all similar compounds dissolve in water without undergoing any other change, and are deposited in their original state by crystallization. When any hydracid, such as muriatic or hydriodic acid, is mixed with potassa or any similar metallic oxide, the acid and salifiable base do not unite, as happens in other cases; but the oxygen of the oxide

combines with the hydrogen of the acid, and the metal itself with the radical of the hydracid. This kind of double decomposition unquestionably takes place in some instances, as when sulphuretted hydrogen acts upon a salt of lead, the insoluble sulphuret of lead being actually precipitated; but it is also by some thought to occur even when the transparency of the solution is undisturbed. According to this view, muriate of potassa, and the salts of the hydracids in general have no existence. When nitrate of the oxide of silver is added to a solution of the chloride or cyanuret of potassium, metallic silver unites with chlorine or cyanogen, while the oxygen of the oxide of silver combines with potassium; so that nitrate of potassa, and chloride or cyanuret of silver are generated. On adding sulphuric acid to a solution of the chloride of potassium, instantaneous production of muriatic acid and potassa ensues, in consequence of water being decomposed, and yielding its hydrogen to chlorine, and its oxygen to potassium; and this explanation is justified by the circumstance, that the same change is admitted to occur when concentrated sulphuric acid is brought into contact with solid chloride of potassium. It is further believed that the crystallized muriates of lime, baryta, and strontia, which contain water or its elements, are metallic chlorides combined with water of crystallization; and the same view is applied to all analogous compounds.

According to the other view, chloride of potassium is converted into muriate of potassa in the act of dissolving; and when the solution is evaporated, the elements existing in the salt reunite at the moment of crystallization, and crystals of the chloride of potassium are deposited. The same explanation applies in all cases, when the salt of a hydracid crystallizes without retaining the elements of water. Of those compounds, which in crystallizing retain water or its elements in combination, two opinions may be formed. Thus crystallized muriate of baryta, which consists of one equivalent of chlorine, one of barium, two of oxygen, and two of hydrogen, may be regarded as a compound either of muriate of baryta with one equivalent of water of crystallization, or of chloride of barium with two equivalents of water. When exposed to heat, two proportionals of water are expelled, and chloride of barium is left. When nitrate of the oxide of silver is mixed in solution with muriate of potassa, the oxygen of the oxide of silver unites with the hydrogen of the muriatic acid; chloride of silver is precipitated, and nitrate of potassa remains in the liquid. On adding sulphuric acid to a muriate, muriatic acid is simply displaced, as when carbonic acid in marble is separated from lime by the action of nitric acid.

On comparing these opinions it is manifest that both are consistent with well known affinities. When, for example, a metallic chloride is dissolved in water, the attraction of chlorine for the metal, and that of oxygen for hydrogen, tend to prevent chemical change; but the affinities of the metal for oxygen, of chlorine for hydrogen, and of muriatic acid for metallic oxides, co-operate in determining the decomposition of water, and the production of a muriate. Neither view has materially the advantage in point of simplicity; for while some phenomena are more simply explained by one mode of reasoning, others are more easily explicable according to the other. It is certainly an objection to the second view, that it supposes the frequent decomposition and reproduction of water, without there being any direct proof of its occurrence; for the solution of chlorides and similar compounds often takes place, even without disengagement of caloric. The circumstances which may be mentioned as appearing to indicate the de-

composition of water, are the following:—1. The solution of some compounds, such as sulphuret and cyanuret of potassium, actually emit an odour of sulphuretted hydrogen and hydrocyanic acid. 2. Other compounds, such as the chlorides of copper, cobalt, and nickel, instantly acquire, when put into water, the colour peculiar to the salts of the oxides of those metals. 3. The solution of protochloride of iron, like the protosulphate, absorbs oxygen from the atmosphere; and this effect could scarcely be expected to occur, unless the protoxide of iron were contained in the liquid. 4. In some instances there is direct proof of decomposition of water. Thus when sulphuret of aluminium is put into that fluid, alumina is generated and sulphuretted hydrogen gas disengaged with effervescence. In like manner the chloride and sulphuret of silicium are converted by water into silica, and muriatic acid and sulphuretted hydrogen. In these cases the want of affinity between the new compounds causes their separation, and thus affords direct proof that water is decomposed. But the affinities which produce this change do not appear so likely to be effective, as those which are in operation when the chloride of potassium is put into water; especially when it is considered that the attraction of chlorine for hydrogen, and potassium for oxygen, is aided by that of the resulting acid and oxide for each other. 5. The last argument I shall mention in favour of this opinion, is founded on the production of the hydrocarburet of iodine by the mutual action of potassa, iodine, and alcohol, as observed by M. Serullas. (page 237.) It was stated at page 212, that when potassa acts on iodine, iodic and hydriodic acids are generated by decomposition of water, and the solution contains the iodate and hydriodate of that alkali. But if the existence of the hydriodate of potassa be denied, the only consistent explanation of the phenomena is, that the elements of potassa unite with separate portions of iodine, producing iodic acid, which unites with undecomposed potassa, and iodide of potassium. According to this view, water is not decomposed at all; whereas the process of M. Serullas does not seem explicable except by the decomposition of water.

The first argument is not perhaps to be trusted, because the production of sulphuretted hydrogen and hydrocyanic acid is probably occasioned by the carbonic acid of the atmosphere. The four latter, though not amounting to demonstration, give a high degree of probability to the existence of salts of muriatic and hydriodic acid; and if this be admitted, the same view may be extended to other hydracids. This opinion, which is preferred by most chemists, except by Berzelius and his pupils, is adopted in the present work. Considering how much the affinity of metals for oxygen, and of the radicals of the hydracids for hydrogen, differs in force, it is likely that some of the chlorides and similar compounds dissolve without change, while others give rise to decomposition of water. But as in general chemists possess no means of determining the nature of the change in particular instances, I have thought it would be most consistent to apply the same view to all, except in some special cases when the contrary is mentioned.

Chemists are acquainted with several metallic phosphurets; and it is probable that phosphorus, like sulphur, is capable of uniting with all the metals. Little attention, however, has hitherto been devoted to these compounds; and for the greater part of our knowledge concerning them we are indebted to the researches of Pelletier. (An. de Chimie, vol. i. and xiii.)

The metallic phosphurets may be prepared in several ways. The most direct method is by bringing phosphorus in contact with metals at a high temperature, or what amounts to the same thing, by igniting metals in contact with phosphoric acid and charcoal. Several of the phosphurets may be formed by passing a current of phosphuretted hydrogen gas over metallic oxides heated to redness in a porcelain tube. Water is generated, and a phosphuret of the metal remains. By similar treatment the chlorides and sulphurets of many metals may be decomposed, and phosphurets formed, provided the metal is capable of retaining phosphorus at a red heat. According to Professor Rose the phosphurets of copper, nickel, cobalt, and iron are the only ones which admit of being advantageously prepared by this method. (Poggendoff's Annalen, vi. 205.) When chlorides are employed, muriatic acid gas, and when sulphurets sulphuretted hydrogen gas, is of course generated.

Phosphorus unites also with some of the metallic oxides. The phosphurets of lime and baryta, for example, may be made by conducting the vapour of phosphorus over those earths at a red heat.

The only metallic carburets of importance are those of iron, which will be described in the section on that metal.

Hydrogen unites with few metals. The only metallic hydrogurets known are those of zinc, potassium, arsenic, and tellurium. No compound of nitrogen and a metal has hitherto been discovered.

The discoveries of modern chemistry have materially added to the number of the metals, especially by associating with them a class of bodies which was formerly believed to be of a nature entirely different. The metallic bases of the alkalies and earths, previous to the year 1807, were altogether unknown; and before that date, the list of metals, with few exceptions, included those only which are commonly employed in the arts, and which are hence often called the common metals. In consequence of this increase in number, it is found convenient for the purpose of description, to arrange them in separate groups; and as the alkalies and earths differ in several respects from the oxides of other metals, it will be convenient to describe them separately. I have accordingly divided the metals into the two following classes:—

Class I. Metals, which by oxidation yield alkalies or earths.

Class II. Metals, the oxides of which are neither alkalies nor earths.

Class I. This class includes 12 metals, which may properly be arranged in three orders.

Order 1. Metallic bases of the alkalies. They are three in number; namely,

Potassium, Sodium, Lithium.

These metals have such a powerful attraction for oxygen, that at common temperatures they decompose water at the moment of contact, and are oxidized with disengagement of hydrogen gas. The resulting oxides are distinguished by their causticity and solubility in water, and by possessing alkaline properties in an eminent degree. They are called *alkalies*, and their metallic bases are sometimes termed *alkaline* or *alkaligenous* metals.

Order 2. Metallic bases of the alkaline earths. These are four in number; namely,

Barium, Strontium, Calcium, Magnesium.

These metals, like the preceding, decompose water rapidly at common temperatures. The resulting oxides are called *alkaline earths*;

because while in their appearance they resemble the earths, they are similar to the alkalies in having a strong alkaline reaction with test paper, and in neutralizing acids. The three first are strongly caustic, and baryta and strontia are soluble in water to a considerable extent.

Order 3. Metallic bases of the earths. These are five in number; namely,

| | | |
|---|---|---|
| Aluminium, | Yttrium, | Silicium. |
| Glucinium, | Zirconium, | |

The oxides of these metals are well known as the pure earths. They are white and of an earthy appearance, in their ordinary state are quite insoluble in water, and do not affect the colour of turmeric or litmus paper. As salifiable bases they are inferior to the alkaline earths. Silica is even considered by several chemists as an acid, and its chemical relations appear to justify the opinion. For reasons to be afterwards mentioned, the propriety of placing silicium among the metals is exceedingly doubtful.

Class II. The number of the metals included in this class amounts to 28. They are all capable of uniting with oxygen, and generally in more than one proportion. Their protoxides have an earthy appearance, but with few exceptions are coloured. They are insoluble in water, and in general do not affect the colour of test paper. Most of them act as salifiable bases in uniting with acids, and forming salts; but in this respect they are much inferior to the alkalies and alkaline earths, by which they may be separated from their combinations. Several of these metals are capable of forming with oxygen compounds, which possess the characters of acids. The metals in which this property has been noticed are manganese, arsenic, chromium, molybdenum, tungsten, antimony, columbium, titanium, tellurium, and gold.

The metals belonging to the second class may be conveniently arranged in the three following orders:—

Order 1. Metals which decompose water at a red heat. They are five in number; namely,

| | | |
|---|---|---|
| Manganese, | Zinc, | Tin. |
| Iron, | Cadmium, | |

Order 2. Metals which do not decompose water at any temperature, and the oxides of which are not reduced to the metallic state by the sole action of heat. Of these there are fifteen in number, namely,

| | | |
|---|---|---|
| Arsenic, | Antimony, | Bismuth, |
| Chromium, | Uranium, | Titanium, |
| Molybdenum, | Cerium, | Tellurium, |
| Tungsten, | Cobalt, | Copper, |
| Columbium, | Nickel, | Lead. |

Order 3. Metals, the oxides of which are decomposed by a red heat. These are

| | | |
|---|---|---|
| Mercury, | Platinum, | Osmium, |
| Silver, | Palladium, | Iridium. |
| Gold, | Rhodium, | |

# CLASS I.

## METALS, WHICH BY OXIDATION YIELD ALKALIES OR EARTHS.

## ORDER I.

### *METALLIC BASES OF THE ALKALIES.*

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## SECTION I.

### *POTASSIUM.*

Potassium was discovered in the year 1807 by Sir H. Davy, and the circumstances which led to the discovery have already been described. (Page 90.) It was prepared by that philosopher by causing the hydrate of potassa, slightly moistened for the purpose of increasing its conducting power, to communicate with the opposite poles of a galvanic battery of 200 double plates; when the oxygen both of the water and the potassa passed over to the positive pole, while the hydrogen of the former, and the potassium of the latter, made their appearance at the negative wire. By this process, potassium is obtained in small quantity only; but Gay-Lussac and Thenard invented a method by which a more abundant supply may be procured. (Recherches Physico-Chimiques, vol. i.) Their process consists in bringing fused hydrate of potassa in contact with turnings of iron heated to whiteness in a gun-barrel. The iron, under these circumstances, deprives the water and potassa of oxygen, hydrogen gas combined with a little potassium is evolved, and pure potassium sublimes, and may be collected in a cool part of the apparatus.

Potassium may also be prepared, as first noticed by M. Curaudau, by mixing dry carbonate of potassa with half its weight of powdered charcoal, and exposing the mixture, contained in a gun-barrel, or spheroidal iron bottle, to a strong heat. An improvement on both processes has been made by M. Brunner, who decomposes potassa by means of iron and charcoal. From eight ounces of fused carbonate of potassa, six ounces of iron filings, and two ounces of charcoal, mixed intimately and heated in an iron bottle, he obtained 140 grains of potassium. (Quarterly Journal, xv. 379.) Berzelius has observed that the potassium thus made, though fit for all the usual purposes to which it is applied, contains a minute quantity of carbon; and, therefore, if required to be quite pure, must be rendered so by distillation in a retort of iron or green glass. A modification of this process has been since described by Wöhler, who effects the decomposition of the potassa solely by means of charcoal. The material employed for the purpose

is carbonate of potassa, prepared by heating cream of tartar to redness in a covered crucible. (Poggendorff's Annalen, iv. 23.)

Potassium is solid at the ordinary temperature of the atmosphere. At 70° it is somewhat fluid, though its fluidity is not perfect till it is heated to 150° F. At 50° it is soft and malleable, and yields like wax to the pressure of the fingers; but it becomes brittle when cooled to 32° F. It sublimes at a red heat without undergoing any change, provided the atmospheric air be completely excluded. Its texture is crystalline, as may be seen by breaking it across while brittle. In colour and lustre, it is precisely similar to mercury. At 60° its density is 0.865, so that it is considerably lighter than water. It is quite opake, and is a good conductor of electricity and caloric.

The most prominent chemical property of potassium is its affinity for oxygen gas. It oxidizes rapidly in the air, or by contact with fluids which contain oxygen. On this account it must be preserved either in glass tubes hermetically sealed, or under the surface of liquids, such as naphtha, of which oxygen is not an element*. If heated in the open air, it takes fire, and burns with a white flame and great evolution of caloric. It decomposes water on the instant of touching it, and so much heat is disengaged, that the potassium is inflamed, and burns vividly while swimming upon its surface. The hydrogen unites with a little potassium at the moment of separation; and this compound takes fire as it escapes, and thus augments the brilliancy of the combustion. When potassium is plunged under water, violent reaction ensues, but without the emission of light, and pure hydrogen gas is evolved.

## *Oxides of Potassium.*

Potassium unites with oxygen in two proportions. The protoxide, commonly called *potash* or *potassa*, is always formed when potassium is put into water, or when it is exposed at common temperatures to dry air or oxygen gas. By the first method the protoxide is obtained in combination with water; and in the latter, it is anhydrous. In performing the last mentioned process, the potassium should be cut into very thin slices; for otherwise the oxidation is incomplete. The product, when partially oxidized, was once suspected to be a distinct oxide; but it is now admitted to be a mixture of potassa and potassium.

As potassa is the protoxide of potassium, it is supposed to contain one atom of each of its elements. Its composition is best determined by collecting and measuring the quantity of hydrogen which is evolved when potassium is plunged under water. From the experiments of Sir H. Davy, and Gay-Lussac and Thenard, it appears that forty grains of potassium decompose precisely nine grains of water; and that while one grain of hydrogen escapes in the gaseous form, the corresponding eight grains of oxygen combine with the metal. The protoxide of potassium is, therefore, composed of

* Mr Durand, Pharmaceutist of Philadelphia, has ascertained that the essential oil of copaiba is a good liquid for the preservation of potassium. I have used it for this purpose for more than a year, and have satisfied myself that it is much superior to the ordinary naphtha. The brightness of the metal is but slightly impaired, while in naphtha, it becomes covered with a blackish film. Several chemists have used the oil on the recommendation of Mr Durand, and with satisfactory results. B.

| | | |
|---|---|---|
| Potassium | . | 40, or one equivalent. |
| Oxygen | . | 8, or one equivalent. |

and its equivalent is 48.

When potassium burns in the open air or in oxygen gas, it is converted into an orange-coloured substance, which is the peroxide of potassium. It may likewise be formed by conducting oxygen gas over potassa at a red heat*. When this peroxide is put into water, it is resolved into oxygen and potassa, the former of which escapes with effervescence, and the latter is dissolved. According to Gay-Lussac and Thenard, it consists of

| | | |
|---|---|---|
| Potassium | . | 40, or one equivalent. |
| Oxygen | . | 24, or three equivalents. |

Anhydrous potassa may be prepared either by the slow oxidation of potassium, as already mentioned, or by decomposing nitrate of potassa by a red heat in a vessel of gold. In its pure state, it is a white solid substance, highly caustic, which fuses at a temperature somewhat above that of redness, and bears the strongest heat of a wind furnace without being decomposed or volatilized. It has a powerful affinity for water, and intense heat is disengaged during the act of combination. With a certain portion of that liquid, it forms a solid hydrate, the elements of which are united by an affinity so energetic, that no degree of heat hitherto employed can effect their separation. This substance was long regarded as the pure alkali, but it is in reality the *hydrate of potassa*. It is composed of 48 parts or one equivalent of potassa, and 9 parts or one equivalent of water.

The hydrate of potassa is solid at common temperatures. It fuses at a heat rather below redness, and assumes a somewhat crystalline texture in cooling. It is highly deliquescent, and requires about half its weight of water for solution. It is soluble, likewise, in alcohol. It destroys all animal textures, and on this account is employed in surgery as a caustic. It was formerly called *lapis causticus*, but it is now termed *potassa* and *potassa fusa* by the Colleges of Edinburgh and London. This preparation is made by evaporating the aqueous solution of potassa in a silver or clean iron capsule to the consistence of oil, and then pouring it into moulds. In this state it is impure, containing oxide of iron, together with the chloride of potassium, and carbonate and sulphate of potassa. It is purified from these substances by dissolving it in alcohol, and evaporating the solution to the same

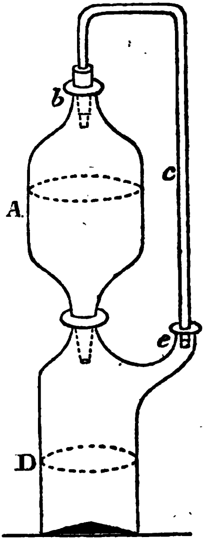
* Peroixde of potassium may be more readily obtained by exposing nitrate of potassa to a red heat, so long as gaseous matter is evolved. Dr Bridges of Philadelphia ascertained this fact in the spring of 1827, while investigating the nature of the gaseous matter given off, on the addition of water, from the residuum of nitre, after exposure in an iron bottle to a red heat. This matter proved to consist of oxygen nearly pure, and the residuum was converted into a solution of hydrate of potassa. These results evidently prove, that the residuum in question consists of peroxide of potassium, mixed, perhaps, with a certain quantity of dry potassa. Dr Bridges suggests that the employment of this residuum might prove convenient to the chemist for obtaining oxygen extemporaneously, as it would be necessary only to add water in order to obtain the gas. *North American Medical and Surgical Journal*, v. 241.

About the same time that Dr Bridges made the above observations, similar ones were made by Mr Phillips in London. *Annals of Philosophy, April* 1827. B.

extent as before, in a silver vessel. The operation should be performed expeditiously, in order to prevent, as far as possible, the absorption of carbonic acid. When the common caustic potassa of the druggists is dissolved in water, a number of small bubbles of gas are disengaged, which are pure oxygen. Mr Graham finds its quantity to be variable in different specimens, and to depend apparently on the impurity of the specimen.

The aqueous solution of potassa, the *aqua potassæ* of the Pharmacopœia, is prepared by decomposing carbonate of potassa by lime. To effect this object completely, it is advisable to employ equal parts of quicklime and carbonate of potassa. After slaking the lime in an iron vessel, the carbonate of potassa, dissolved in its own weight of hot water, is added, and the mixture boiled briskly for about ten minutes. The liquid, after subsiding, is filtered through a funnel, the throat of which is obstructed by a piece of clean linen. This process is founded on the fact that lime deprives carbonate of potassa of its acid, forming an insoluble carbonate of lime, and setting the pure alkali at liberty. If the decomposition is complete, the filtered solution should not effervesce when neutralized with an acid.

As pure potassa absorbs carbonic acid rapidly when freely exposed to the atmosphere, it is desirable to filter its solution in vessels containing as small a quantity of air as possible. This is easily effected by means of the filtering apparatus devised by Mr Donovan. It consists of two vessels A and D, of equal capacity, and connected with each other as represented in the annexed wood cut. The neck *b* of the upper vessel contains a tight cork, perforated to admit one end of the glass tube *c*, and the lower extremity of the same vessel terminates in a funnel pipe, which fits into one of the necks of the under vessel D by grinding, luting, or by a tight cork. The vessel D is furnished with another neck *e*, which receives the lower end of the tube *c*, the junction being secured by means of a perforated cork, or luting. The throat of the funnel pipe is obstructed by a piece of coarse linen loosely rolled up, and not pressed down into the pipe itself. The solution is then poured in through the mouth at *b*, the cork and tube having been removed; and the first droppings, which are turbid, are not received in the lower vessel. The parts of the apparatus are next joined together, and the filtration may proceed at the slowest rate, without exposure to more air than was contained in the vessels at the beginning of the process. This apparatus should be made of green in preference to white glass, as the pure alkalies act on the former much less than on the latter. (Annals of Philosophy, xxvi. 115.)




The mode by which this apparatus acts scarcely needs explanation. In order that the liquid should descend freely, two conditions are required;—first, that the air above the liquid should have the same elastic force, and therefore exert the same pressure, as that below; and, secondly, as one means of securing the first condition, that the air should have free egress from the lower vessel. Both objects, it is

manifest, are accomplished in the filtering apparatus of Mr Donovan; since for every drop of liquid which descends from the upper to the lower vessel, a corresponding portion of air passes along the tube *c* from the lower vessel to the upper.

The solution of potassa is highly caustic, and its taste intensely acrid. It possesses alkaline properties in an eminent degree, converting the vegetable blue colours to green, and neutralizing the strongest acids. It absorbs carbonic acid gas rapidly, and is consequently employed for withdrawing that substance from gaseous mixtures. For the same reason it should be preserved in well-closed bottles, that it may not absorb carbonic acid from the atmosphere.

Potassa is employed as a re-agent in detecting the presence of bodies, and in separating them from one another. The solid hydrate, owing to its strong affinity for water, is used for depriving gases of hygrometic moisture, and is admirably fitted for forming frigorific mixtures. (Page 53.)

Potassa may be distinguished from all other substances by the following characters. 1. If tartaric acid be added in excess to a salt of potassa dissolved in water, and the solution be stirred with a glass rod, a white precipitate, the bitartrate of potassa, soon appears, which forms peculiar white streaks upon the glass by the pressure of the rod in stirring. 2. A solution of muriate of platinum causes a yellow precipitate, the muriate of platinum and potassa. This is the most delicate test, provided the mixture be gently evaporated to dryness, and a little cold water be afterwards added. The muriate of platinum and potassa then remains in the form of small shining yellow crystals. 3. By being precipitated by no other substance.

*Chloride of Potassium.*—Potassium takes fire spontaneously in an atmosphere of chlorine, and burns with greater brilliancy than in oxygen gas. This chloride is also generated when potassium is heated in muriatic acid gas, hydrogen being evolved at the same time. It is the residue of the decomposition of chlorate of potassa by heat; and it is obtained in the form of colourless cubic crystals, when a solution of the muriate of potassa evaporates spontaneously.

Chloride of potassium has a saline and rather bitter taste. It requires three parts of water at 60° F. for solution, and is rather more soluble in hot water. Its solution probably contains the muriate of potassa. (Page 275.) It is composed of 36 parts, or one equivalent of chlorine, and 40 parts, or one equivalent of potassium.

*Iodide of Potassium.*—This compound is formed with emission of light, when potassium is heated in contact with iodine. It may likewise be obtained by means of heat from the iodate, and by crystallization from the hydriodate of potassa. It fuses readily when heated, and is volatilized at a temperature below redness. It deliquesces in a moist atmosphere, and is very soluble in water. It dissolves also in strong alcohol; and the solution, when gently evaporated, yields small colourless cubic crystals of the iodide of potassium. It is composed of 124 parts, or one equivalent of iodine, and 40 parts, or one equivalent of potassium.

*Hydrogen and Potassium.*—These substances unite in two proportions, forming in one case a solid, and in the other a gaseous compound. The latter is produced when hydrate of potassa is decomposed by iron at a white heat, and it appears also to be generated when potassium burns on the surface of water. It inflames spontaneously in air or oxygen gas; but on standing for some hours over mercury, the greater part, if not the whole of the potassium, is deposited.

The solid hydroguret of potassium was made by Gay-Lussac and Thenard, by heating potassium in hydrogen gas. It is a gray solid substance, which is readily decomposed by heat or contact with water. It does not inflame spontaneously in oxygen gas.

*Sulphuret of Potassium.*—Sulphur unites readily with potassium by the aid of heat; and so much caloric is evolved at the moment of combination, that the mass becomes incandescent. The best method of obtaining a sulphuret in definite proportion is by decomposing sulphate of potassa according to the process of Berthier or Berzelius. (Page 274.) This sulphuret is composed of 16 parts, or one equivalent of sulphur, and 40 parts, or one equivalent of potassium. It has a red colour, fuses below the temperature of ignition, and assumes a crystalline texture in cooling. It is dissolved by water, being probably converted, with evolution of caloric, into the hydrosulphuret of potassa.

Besides this protosulphuret, Berzelius has described four other compounds, which he obtained by igniting carbonate of potassa with different proportions of sulphur. These are composed of one equivalent of potassium to two, three, four, and five equivalents of sulphur.

*Phosphuret of Potassium.*—This compound may be formed by the action of potassium on phosphorus with the aid of a moderate heat. It is converted by water into potassa and perphosphuretted hydrogen gas, which inflames at the moment of its formation.

## SECTION II.

### *SODIUM.*

Sir H. Davy made the discovery of sodium in the year 1807, a few days after he had discovered potassium. The first portions of it were obtained by means of galvanism; but it may be procured in much larger quantity by chemical processes, precisely similar to those described in the last section.

Sodium has a strong metallic lustre, and in colour is very analogous to silver. It is so soft at common temperatures, that it may be formed into leaves by the pressure of the fingers. It fuses at 200° F. and rises in vapour at a full red heat. Its specific gravity is 0.972.

Sodium soon tarnishes on exposure to the air, though less rapidly than potassium. When thrown into water, it swims upon its surface, occasions violent effervescence and a hissing noise, and is rapidly oxidized; but no light is visible. The action is stronger with hot water, and a few scintillations appear; but still there is no flame.* In each case, soda is generated, owing to which the water acquires an alkaline reaction, and pure hydrogen gas is disengaged.

* The sodium, which I have had occasion to use, uniformly inflames on boiling water. The experiment is a very beautiful one, and deserves the attention of chemical lecturers. This fact I obtained in conversation with Mr D. B. Smith, and I do not now recollect to have seen it mentioned in any chemical work, except Professor Silliman's Outlines. It may be supposed that the inflammation of the metal is owing to the presence of potassium; but this is not probable, as the flame is of a fine yellow colour, very different from the rose colour of the flame of potassium. B.

*Oxides of Sodium.*—Chemists are acquainted with two definite compounds only of sodium and oxygen. The protoxide, or soda, is a gray white solid, difficult of fusion, which is obtained by burning sodium in dry atmospheric air. It is also formed when sodium is oxidized by water; and its composition may be determined by collecting the hydrogen which is then disengaged. According to the experiments of Sir H. Davy, the results of which differ little from those of Gay-Lussac and Thenard, soda consists of 24 parts of sodium and 8 parts of oxygen. For this reason, 24 is regarded as the atomic weight of sodium, and 32 the combining proportion of soda.

When sodium is strongly heated in excess of pure oxygen, an orange-coloured substance is formed, which is the peroxide of sodium. It is resolved by water into oxygen and soda; and is composed, according to Gay-Lussac and Thenard, of two equivalents of sodium and three of oxygen.

With water soda forms a solid hydrate, easily fusible by heat, which is very caustic, soluble in water and acohol, has powerful alkaline properties, and in all its chemical relations is exceedingly analogous to potassa. It is prepared from the solution of pure soda, exactly in the same manner as the corresponding preparation of potassa. The solid hydrate is composed of 32 parts or one equivalent of soda, and 9 parts or one equivalent of water.

Soda is readily distinguished from other alkaline bases by the following characters. 1. It yields with sulphuric acid a salt, which by its taste and form is easily recognised as Glauber's salt or sulphate of soda. 2. All its salts are soluble in water, and are not precipitated by any reagent. 3. On exposing its salts by means of platinum wire to the blowpipe flame, they communicate to it a rich yellow colour.

*Chloride of Sodium.*—This compound may be formed directly by burning sodium in chlorine, or by heating it in muriatic acid gas. It is deposited in crystals, when a solution of muriate of soda is evaporated; for this salt, like muriate of potassa, exists only while in solution, and is converted into a chloride during the act of crystallizing. Hence sea water, the chief ingredient of which is muriate of soda, yields chloride of sodium by evaporation; and from this source is derived most of the different kinds of common salt, such as fishery salt, stoved salt, and bay salt, substances essentially the same, and between which the sole difference depends on the mode of preparation. Chloride of sodium is known likewise as a natural product under the name of rock or mineral salt.

The common varieties of salt, of which rock and bay salt are the purest, always contain small quantities of sulphate of magnesia and lime, and muriate of magnesia. These earths may be precipitated as carbonates by boiling a solution of salt for a few minutes with a slight excess of carbonate of soda, filtering the liquid, and neutralizing with muriatic acid. On evaporating this solution rapidly, chloride of sodium crystallizes in hollow four-sided pyramids; but it occurs in regular cubic crystals when the solution is allowed to evaporate spontaneously. These crystals contain no water of crystallization, but decrepitate remarkably when heated, owing to the expansion of water mechanically confined within them.

Pure chloride of sodium has an agreeably saline taste. It fuses at a red heat, and becomes a transparent brittle mass on cooling. It deliquesces slightly in a moist atmosphere, but undergoes no change when the air is dry. In pure alcohol it is insoluble. It requires twice and a half its weight of water at 60° F. for solution, and its solubility

is not increased by heat. Like the soluble chlorides in general, it passes into a muriate while in the act of dissolving. (Page 275.) Sulphuric acid decomposes it with evolution of muriatic acid gas, and formation of sulphate of soda. In composition it is analogous to the chloride of potassium, consisting of one equivalent of chlorine, and one of sodium.

The uses of chloride of sodium are well known. Besides its employment in seasoning food, and in preserving meat from putrefaction, a property which when pure it possesses in a high degree, it is used for various purposes in the arts, especially in the formation of muriatic acid and chloride of lime.

The compounds of sodium with iodine, sulphur, and phosphorus are so analogous to those which potassium forms with the same elements, that a particular description of them is unnecessary. Sodium does not unite with hydrogen.

*Chloride of Soda.*—This compound has lately acquired the attention of scientific men under the name of Labarraque's *disinfecting soda liquid*, which was announced by M. Labarraque as a compound of chlorine and soda, analogous to the well known bleaching powder, chloride of lime. The nature of this liquid has been since investigated by Mr Phillips and Mr Faraday, especially by the latter; and it appears from the experiments of this chemist, that while chloride of soda is the active ingredient, its properties are considerably modified by the presence of carbonate of soda. (Quarterly Journal of Science, N. S. ii. 84.)

Pure chloride of soda is easily prepared by transmitting to saturation a current of chlorine gas into a cold and rather dilute solution of caustic soda. Common carbonate of soda may be substituted for the pure alkali; but considerable excess of chlorine must then be employed in order to displace the whole of the carbonic acid. It may also be formed easily, cheaply, and of uniform strength, by decomposing chloride of lime with carbonate of soda, as proposed by M. Payen. (Quarterly Journal of Science, N. S. i. 236.) However prepared, its properties are the same. As its constituents are retained in combination by a feeble affinity, the compound is easily destroyed. It emits an odour of chlorine, and possesses the bleaching properties of that substance in a very high degree. When kept in open vessels, it is slowly decomposed by the carbonic acid of the atmosphere with evolution of chlorine; and the change is more rapid in air charged with putrid effluvia, because the carbonic acid produced during putrefaction promotes the decomposition of the chloride. On this, as was proved by M. Gaultier de Claubry, depends the efficacy of an alkaline chloride in purifying air loaded with putrescent exhalations. When the solution is heated to the boiling point, or concentrated by means of heat, the chloride undergoes a change previously explained, (page 197,) and is converted into chlorate and muriate of soda.

Chloride of soda may be employed in bleaching, and for all purposes to which chlorine gas or its solution was formerly applied. It is now much used in removing the offensive odour arising from drains, sewers, or all kinds of animal matter in a state of putrefaction. Bodies disinterred for the purpose of judicial inquiry, or parts of the body advanced in putrefaction, may by its means be rendered fit for examination; and it is employed in surgical practice for destroying the fetor of malignant ulcers. Clothes worn by persons during pestilential diseases are disinfected by being washed with this compound. It is also used in fumigating the chambers of the sick; for the disengagement of chlorine is so gradual, that it does not prove injurious or

annoying to the patient. In all these instances, chlorine appears actually to decompose noxious exhalations by uniting with the elements of which they consist, and especially with hydrogen.

In preparing the disinfecting liquid of Labarraque, it is necessary to be exact in the proportion of the ingredients employed. The quantities used by Mr Faraday, founded on the directions of Labarraque, are the following: He dissolved 2800 grains of crystallized carbonate of soda in 1.28 pints of water, and through the solution, contained in a Woulfe's apparatus, was transmitted the chlorine, evolved from a mixture of 967 grains of sea-salt and 750 grains of peroxide of manganese, when acted on by 967 grains of sulphuric acid, diluted with 750 grains of water. In order to remove any accompanying muriatic acid gas, the chlorine before reaching the soda was conducted through pure water, by which means nearly a third part was dissolved, but the remaining two-thirds were fully sufficient for the purpose. The gas was readily absorbed by the solution, and from the beginning to the end of the process, not a particle of carbonic acid gas was evolved; whereas by employing an excess of chlorine, the carbonic acid may be entirely expelled.

The solution thus prepared has all the characters of Labarraque's soda liquid. Its colour is a pale yellow, and it has but a slight odour of chlorine. Its taste is at first sharp, saline, and scarcely at all alkaline; but it produces a persisting biting effect upon the tongue. It first reddens and then destroys the colour of turmeric paper. When boiled it does not give out chlorine, nor is its bleaching power perceptibly impaired; and if carefully evaporated, it yields a mass of damp crystals, which, when redissolved, bleach almost as powerfully as the original liquid. When rapidly evaporated to dryness, the residue contains scarcely any chlorate of soda or chloride of sodium; but it has nevertheless lost more than half of its bleaching power, and therefore chlorine must have been evolved during the evaporation. The solution deteriorates gradually by keeping, chloric acid and chloride of sodium being generated. When allowed to evaporate spontaneously, chlorine gas is gradually evolved, and crystals of carbonate of soda remain.

In some respects the nature of this liquid is still obscure; but from the preceding facts, drawn from the essay of Mr Faraday, two points seem to be established. First, that the liquid contains chlorine, carbonic acid, and soda. Secondly, that the chlorine is not simply combined either with water or soda; for by boiling, the gas is neither expelled as it would be from an aqueous solution, nor does the liquid yield chloric acid and chloride of sodium as when pure chloride of soda is heated. It may perhaps be regarded as a compound of chloride of soda and bicarbonate of soda. Its production may be conceived by supposing, that when chlorine is introduced in due quantity into a solution of carbonate of soda, it combines with half of the alkali, while the remainder with all the carbonic acid constitutes bicarbonate of soda. Should this salt unite, though by a feeble affinity, with chloride of soda, both may thence derive a degree of permanence, which neither singly possesses. During spontaneous evaporation, the tendency of the common carbonate to crystallize may occasion its reproduction, and the disengagement of chlorine. These remarks, however, are merely speculative.

# SECTION III.

## *LITHIUM.*

In the year 1818, M. Arfwedson of Sweden*, in analyzing the mineral called petalite, discovered the existence of a new alkali, and its presence has since been detected in spodumene, lepidolite, and in several varieties of mica. Berzelius has found it also in the waters of Carlsbad in Bohemia. From the circumstance of its having been first obtained from an earthy mineral, Arfwedson gave it the name of *lithion* (from λιθειος *lapideus*,) a term since changed in this country to *lithia.* It has hitherto been procured in small quantity only, because spodumene and petalite are rare, and do not contain more than 6 or 8 per cent of the alkali. It is combined in these two minerals with silica and alumina, whereas potassa is likewise present in lepidolite and lithion-mica, and therefore lithia should be prepared solely from the former.

The best process for preparing lithia is that which was suggested by Berzelius. One part of petalite or spodumene, in fine powder, is mixed intimately with two parts of fluor spar, and the mixture is heated with three or four times its weight of sulphuric acid, as long as any acid vapours are disengaged. The silica of the mineral is attacked by hydrofluoric acid, and dissipated in the form of fluosilicic acid gas, while the alumina and lithia unite with sulphuric acid. After dissolving these salts in water, the solution is boiled with pure ammonia to precipitate the alumina, filtered, evaporated to dryness, and then heated to redness to expel the sulphate of ammonia. The residue is pure sulphate of lithia†.

Sir H. Davy succeeded, by means of galvanism, in obtaining a white coloured metal like sodium from lithia; but it was oxidized, and thus reconverted into the alkali, with such rapidity that it could not be collected. Lithia may, therefore, be regarded as the protoxide of *lithium*; and, according to the analysis of sulphate of lithia by Stromeyer and Thomson, lithia is inferred to be composed of

| | | |
|---|---|---|
| Lithium . . | 10 | or one proportional. |
| Oxygen . . | 8 | or one proportional. |

Consequently, its combining proportion is 18.

Lithia is distinguished from potassa and soda by its greater neutralizing power, by forming sparingly soluble salts with carbonic and phosphoric acids, and by the circumstance of the chloride of lithium being highly deliquescent, and dissolving freely in strong alcohol. This alcoholic solution burns with a red flame; and all the salts of lithia, when heated on platinum wire before the blowpipe, tinge the flame of a red colour. Further, when lithia is fused on platinum foil, it attacks that metal, and leaves a dull yellow trace round the spot on which it lay. (Berzelius on the Blowpipe. Children's Translation.)

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* An. de Ch. et de Ph. vol. x.

† The sulphate of lithia may be decomposed by acetate of baryta, and the acetate of lithia thus obtained, by exposure to a red heat, is converted into the carbonate. The carbonate may then be brought to the state of a caustic hydrate by the action of lime in the usual manner. B.

Lithia is distinguished from the alkaline earths by forming soluble salts with sulphuric and oxalic acids; and by the circumstance that carbonate of lithia, though sparingly soluble in water, forms with it a solution which gives a brown stain to turmeric paper.

# CLASS I.

## ORDER II.

### *METALLIC BASES OF THE ALKALINE EARTHS.*

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## SECTION IV.

### *BARIUM.*

Sir H. Davy discovered *barium*, the metallic base of baryta, in the year 1808, by a process suggested by Berzelius and Pontin. It consists in forming carbonate of baryta into a paste with water, and placing a globule of mercury in a little hollow made in its surface. The paste was laid upon a platinum tray which communicated with the positive pole of a galvanic battery of 100 double plates, while the negative wire was brought into contact with the mercury. The baryta was decomposed, and its barium entered into combination with mercury. This amalgam was then heated in a vessel free from air, by which means the mercury was expelled, and barium obtained in a pure form.

Barium, thus procured, is of a dark gray colour, with a lustre inferior to cast iron. Its specific gravity is far greater than water, for it sinks rapidly in strong sulphuric acid. It attracts oxygen with avidity from the air, and in doing so yields a white powder which is baryta. It effervesces strongly, from the escape of hydrogen gas, when thrown into water, and a solution of batyta is produced. It has hitherto been obtained in very minute quantities, and consequently its properties have not been determined with precision.

*Oxides of Barium. Barytes*, or *Baryta*, so called from the great density of its compounds, (from βαρὺς heavy) was discovered in the year 1774 by Scheele. It is the sole product of the oxidation of barium in air or water. It may be prepared by decomposing nitrate of baryta at a red heat; or, as was ascertained by Dr Hope, by exposing carbonate of baryta, contained in a black lead crucible, to an intense white heat; a process which succeeds much better, when the carbonate is intimately mixed with charcoal. Baryta is a gray powder, the specific gravity of which is about 4. It requires a very high temperature for fusion. It has a sharp caustic alkaline taste, converts vegetable blue colours to green, and neutralizes the strongest acids. Its alkalinity, therefore, is equally distinct as that of potassa or soda; but it is much less caustic and less soluble in water than those alkalies. In pure alcohol it is insoluble. It has an exeedingly strong affinity for water. When mixed with that liquid it slakes in the same manner as quick-

lime, but with the evolution of a more intense heat, which, according to Döbereiner, sometimes amounts to luminousness. The result is a white bulky hydrate, fusible at a red heat, and which bears the highest temperature of a smith's forge without parting with its water. It is composed of 78 parts or one equivalent of baryta, and 9 parts or one equivalent of water.

The hydrate of baryta dissolves in twice its weight of boiling water, and in twenty parts of water at the temperature of 60° F. (Davy.) A saturated solution of baryta in boiling water deposites, in cooling, transparent, flattened prismatic crystals, which are composed, according to Mr Dalton, of 78 parts or one equivalent of baryta, and 180 parts or twenty equivalents of water.

The aqueous solution of baryta is an excellent test of the presence of carbonic acid in the atmosphere or in other gaseous mixtures. The carbonic acid unites with the baryta, and a white insoluble precipitate, carbonate of baryta, subsides.

The exact combining proportion of barium is not known with certainty; for while Dr Thomson estimates its equivalent at 70, Berzelius states it at 68.66. I have reason to believe neither of these numbers precisely correct; but until the subject shall be decided by future research, I shall continue to use the number stated by Dr Thomson, which is generally employed in this country. Accordingly, baryta is regarded as a compound of 70 parts or one equivalent of barium, and 8 parts or one equivalent of oxygen.

The deutoxide of barium may be formed by conducting dry oxygen gas over pure baryta at a low red heat. An easier process, recommended by M. Quesneville, junr, is to introduce nitrate of baryta into a luted retort of porcelain, to which is attached a Welter's safety tube, terminating under an inverted jar full of water. Heat is gradually applied to the retort, and a red heat continued as long as there is any disengagement of nitric oxide or nitrogen gas. When these have ceased and pure oxygen passes over, which is a proof of all the nitrate being decomposed, the process is discontinued. The peroxide of barium is then found in the retort. This deutoxide, according to Thenard, contains twice as much oxygen as baryta; or is composed of one equivalent of barium and two equivalents of oxygen. This is the substance employed by Thenard in the formation of the deutoxide of hydrogen.

Baryta is distinguished from all other substances by the following characters. 1. By dissolving in water and forming an alkaline solution. 2. By all its soluble salts being precipitated as the white carbonate of baryta by alkaline carbonates, and as sulphate of baryta, which is insoluble both in acid and alkaline solutions, by sulphuric acid or any soluble sulphate. 3. By forming with muriatic acid a salt, which crystallizes readily by evaporation in the form of four, six, or eight-sided tables, is insoluble in alcohol, and does not undergo any change on exposure to the air.

The readiest method of forming the salts of baryta is by the action of moderately dilute acids on the native or artificial carbonate.

All the soluble salts of baryta are poisonous. The carbonate of baryta, from being dissolved by the juices of the stomach, likewise acts as a poison. The sulphate, from its perfect insolubility, is inert.

*Chloride of Barium.*—This compound is generated when chlorine gas is conducted over baryta at a red heat, and oxygen gas is disengaged. It may also be formed by heating to redness the crystallized muriate of baryta. It consists of one equivalent of each of its constituents. It requires five times its weight of water at 60° F. for solution, and is much more soluble in boiling water.

*Sulphuret of Barium.*—The protosulphuret of barium may be prepared from sulphate of baryta by the action of charcoal or hydrogen gas at a high temperature. (Page 274.) It dissolves readily in hot water, forming the hydrosulphuret of baryta. By means of this solution all the chief salts of baryta may be procured. Thus, by adding an alkaline carbonate, carbonate of baryta is precipitated; and when muriate acid is added, sulphuretted hydrogen is evolved, and muriate of baryta produced. A solution of pure baryta may also be obtained from the hydrosulphuret, by boiling it with peroxide of copper, until the filtered solution no longer gives a dark precipitate with acetate of lead. The crystallized hydrate of baryta is easily procured by means of this solution.

The combinations of barium with the other non-metallic substances have not yet been carefully examined.

## SECTION V.

### *STRONTIUM.*

The metallic base of strontia, called *strontium*, was discovered by Sir H. Davy by a process analogous to that described in the last section. All that is known respecting its properties is, that it is a heavy metal, similar in appearance to barium, that it decomposes water with evolution of hydrogen gas, and oxidizes quickly in the air, being converted in both cases into strontia.

From the close resemblance between baryta and strontia, these substances were once supposed to be identical. Dr Crawford, however, and M. Sulzer noticed a difference between them; but the existence of strontia was first established with certainty in the year 1792 by Dr Hope*, and the same discovery was made about the same time by Klaproth†. It was originally extracted from strontianite, the native carbonate of strontia, a mineral found at Strontian in Scotland; and hence the origin of the term *strontites* or *strontia*, by which the earth itself is designated.

Pure strontia may be prepared from nitrate and carbonate of strontia, in the same manner as baryta. It resembles this earth in appearance, in infusibility, and in possessing distinct alkaline properties. It slakes when mixed with water, causing intense heat, and forming a white solid hydrate, which consists of 52 parts or one equivalent of strontia, and 9 parts or one equivalent of water. The hydrate of strontia fuses readily at a red heat, but sustains the strongest heat of a wind furnace without decomposition. It is insoluble in alcohol. Boiling water dissolves it freely, and a hot saturated solution, on cooling, deposites transparent crystals in the form of thin quadrangular tables. These crystals are composed, according to the analysis of Dr Hope, of 52 parts or one equivalent of strontia, and 108 parts or twelve equivalents of water. They are converted by heat into the proto-hydrate. They require 50 times their weight of water at 60° F. for solution, and twice their weight at 212° F. (Dalton.)

* Edinburgh Philosophical Transactions, iv. 3.

† Klaproth's Contributions, vol. i.

The solution of strontia has a caustic taste and alkaline reaction. Like the solution of baryta, it is a delicate test of the presence of carbonic acid in air or other gaseous mixtures, forming with it the insoluble carbonate of strontia.

The atomic weight of strontia, as deduced from the analyses of Berzelius, Stromeyer, and Thomson, is 52; and consequently strontia, regarded as the protoxide of strontium, is composed of

| | | | |
|---|---|---|---|
| Strontium | . | 44 | or one proportional. |
| Oxygen | . | 8 | or one proportional. |

The deutoxide of strontium is prepared in the same manner as the corresponding preparation of baryta. It may likewise be formed by pouring an aqueous solution of strontia into the deutoxide of hydrogen. According to Thenard, it contains twice as much oxygen as the protoxide.

The soluble salts of strontia, like those of baryta, are precipitated by alkaline carbonates, and by sulphuric acid or soluble sulphates. Strontia is distinguished from baryta by forming with muriatic acid a salt, which crystallizes in the form of slender hexagonal prisms, deliquesces in a moist atmosphere, and dissolves freely in pure alcohol. The alcoholic solution, when set on fire, burns with a blood-red flame; and the salts of strontia, when exposed to the blowpipe flame on platinum wire, impart to it a red tinge. They are also distinguished by a difference in the solubility of their sulphates. On adding Glauber's salt in excess to a soluble salt of baryta, that base is so completely precipitated, that its presence cannot be afterwards detected in the solution by any re-agent. But when a salt of strontia is thus treated, so much sulphate of strontia remains in solution, that the filtered liquid yields a white precipitate with carbonate of potassa or soda.

The salts of strontia are most conveniently prepared from the carbonate. These compounds are not poisonous.

The chloride of strontium is formed under precisely the same circumstances as the chloride of barium, and its composition is analogous. It is exceedingly soluble in boiling water, and requires twice its weight of water at 60° F. for solution. As already mentioned, it is soluble in alcohol.

The sulphuret of strontium may be prepared by the processes referred to in the last section. It may be advantageously employed for forming the solution and salts of strontia, in the same manner as those of baryta are prepared from the sulphuret of barium. It consists of 44 parts or one equivalent of strontium, and 16 parts or one equivalent of sulphur.

## SECTION VI.

### *CALCIUM.*

The existence of calcium, the metallic base of lime, was demonstrated by Sir H. Davy by a process similar to that described in the section on barium. It is of a whiter colour than barium or strontium, and is converted into lime by being oxidized. Its other properties are unknown.

When carbonate of lime is exposed to a white or even to a very strong

red heat, carbonic acid is expelled, and pure lime, commonly called *quicklime*, remains. If lime of great purity is required, it should be prepared from pure carbonate of lime, such as Iceland-spar, or Carrara marble; but in burning lime in lime-kilns for making mortar, common lime-stone is employed. The expulsion of carbonic acid is facilitated by mixing the carbonate with combustible substances, in which case carbonic oxide is generated. (Page 176.)

Lime is a brittle, white, earthy solid, the specific gravity of which is about 2.3. It phosphoresces powerfully when heated to full redness, a property which it possesses in common with strontia and baryta. It is one of the most infusible bodies known; fusing with difficulty, even by the heat of the oxy-hydrogen blowpipe. It has a powerful affinity for water, and the combination is attended with great increase of temperature, and formation of a white bulky hydrate, which is composed of 28 parts or one equivalent of lime, and 9 parts or one equivalent of water. The process of *slaking* lime consists in forming this hydrate, and the hydrate itself is called *slaked* lime. It differs from the hydrates of strontia and baryta in parting with its water at a red heat.

The hydrate of lime is dissolved very sparingly by water, and it is a singular fact, first noticed, I believe, by Mr Dalton, that it is more soluble in cold than in hot water. Thus he found that one grain of lime requires for solution

| | |
|---|---|
| 778 grains of water . | at 60° F. |
| 972 . . . | 180° |
| 1270 . . . | 212° |

And, consequently, on heating a solution of lime, or *lime-water*, which has been prepared in the cold, deposition of lime ensues. This fact was determined experimentally by Mr Phillips, who has likewise observed that water at 32° F. is capable of dissolving twice as much lime as at 212° F.

Owing to this circumstance pure lime cannot be made to crystallize in the same manner as baryta or strontia. Gay-Lussac succeeded, however, in obtaining crystals of lime by evaporating lime-water, under the exhausted receiver of an air-pump, by means of sulphuric acid, as in Mr Leslie's process for freezing water. (Page 60.) Small transparent crystals, in the form of regular hexahedrons, are deposited, which consist of water and lime in the same proportion as in the hydrate above mentioned.

Lime-water is prepared by mixing hydrate of lime with water, agitating the mixture repeatedly, and then setting it aside in a well-stopped bottle until the undissolved parts shall have subsided. The substance called *milk* or *cream* of lime is made by mixing hydrate of lime with a sufficient quantity of water to give it the liquid form;—it is merely lime-water in which hydrate of lime is mechanically suspended.

Lime-water has a harsh acrid taste, and converts vegetable blue colours to green. It agrees, therefore, with baryta and strontia in possessing distinct alkaline properties. Like the solution of these earths, it has a strong affinity for carbonic acid, and forms with it an insoluble carbonate. On this account, lime-water should be carefully protected from the air. For the same reason, lime-water is rendered turbid by a solution of carbonic acid; but on adding a large quantity of the acid, the transparency of the solution is completely restored, because carbonate of lime is soluble in an excess of carbonic acid. The action of this acid on the solutions of baryta and strontia is precisely similar.

The atomic weight of lime, as deduced from the experiments of Dr Thomson, is 28; and therefore lime, regarded as the protoxide of calcium, is composed of 20 parts or one equivalent of calcium, and 8 parts or one equivalent of oxygen.

The deutoxide of calcium may be formed in the same way as the deutoxide of strontium. According to Thenard, it consists of one equivalent of calcium and two equivalents of oxygen.

The salts of lime, which are easily prepared by the action of acids on pure marble, are in many respects similarly affected by reagents, as those of baryta and strontia. They are precipitated, for example, by alkaline carbonates. Sulphuric acid and soluble sulphates likewise precipitate lime from a moderately strong solution. But sulphate of lime has a considerable degree of solubility. Thus, a dilute solution of a salt of lime is not precipitated at all by sulphuric acid; and when the sulphate of lime is separated, it may be redissolved by the addition of nitric acid.

The most delicate test of the presence of lime is oxalate of ammonia or of potassa; for of all the salts of lime, the oxalate is the most insoluble in water. This serves to distinguish lime from most substances, though not from baryta and strontia; because the oxalates of baryta and strontia, especially the latter, are likewise sparingly soluble. All these oxalates dissolve readily in water acidulated with nitric or muriatic acid.

The best characters for distinguishing lime from baryta and strontia are the following:—Nitrate of lime yields prismatic crystals by evaporation, is deliquescent in a high degree, and very soluble in alcohol. The nitrates of baryta and strontia crystallize in regular octahedrons or segments of an octahedron, undergo no change on exposure to the air, except when very moist, and do not dissolve in pure alcohol.

The salts of lime, when heated before the blowpipe, or when their solutions in alcohol are set on fire, communicate to the flame a dull brownish-red colour.

*Chloride of Calcium.*—The chloride of calcium is formed in the same manner as chloride of strontium. In decomposing muriate of lime by heat, a little muriatic acid is sometimes expelled as well as water. Chloride of calcium is soluble in alcohol, and deliquesces rapidly on exposure to the atmosphere. On account of its strong affinity for water, it is much employed to deprive gases and other substances of their moisture. For a like reason, it may be used for forming frigorific mixtures with snow; but for this purpose the crystallized muriate of lime, which contains six equivalents of water of crystallization, is far preferable.

Chloride of calcium contains one proportional of each of its elements.

*Chloride of Lime.*—This compound, commonly called *oxymuriate of lime*, or *bleaching powder*, is prepared by exposing thin strata of recently slaked lime in fine powder to an atmosphere of chlorine. The gas is absorbed in large quantity, and combines directly with the lime.

Chloride of lime is a dry white powder, which smells faintly of chlorine, and has a strong taste. It dissolves partially in water, and the solution possesses powerful bleaching properties, and contains both chlorine and lime; while the undissolved portion is hydrate of lime, retaining a small quantity of chlorine. The aqueous solution, when exposed to the atmosphere, is gradually decomposed;—chlorine is set free, and carbonate of lime generated. On boiling the liquid, muriatic, and I presume chloric, acid are formed; and by long keep-

ing, the dry chloride appears to undergo a similar change, at least muriatic acid is produced in large quantity. The chloride of lime is also decomposed by a strong heat. At first, chlorine is evolved; but pure oxygen is afterwards disengaged, and chloride of calcium remains in the retort.

The composition of chloride of lime was first carefully investigated by Mr Dalton,* and it has since been analyzed by Dr Thomson,† M. Welter,‡ and Dr Ure.§ The three first mentioned chemists infer from their researches that the bleaching powder is a hydrated *sub-chloride* or *di-chloride* of lime, in which 36 parts or one equivalent of chlorine are united with 56 parts or two equivalents of lime. They are also of opinion that, on mixing the sub-chloride with water, a real chloride is dissolved, and one equivalent of lime separated as an insoluble powder. Dr Ure, on the contrary, denies that the bleaching powder is a sub-chloride; and maintains, according to the result of his own analysis, that the elements of this compound do not constitute a regular atomic combination. He found that the quantity of chlorine absorbed by hydrate of lime is variable, depending not only on the pressure and degree of exposure, but on the quantity of water which is present. The following is the result of his analysis of three specimens, No. 1 being good commercial bleaching powder, No. 2 made by himself with pure proto-hydrate of lime, and No. 3 prepared by himself with lime containing more water than in No. 2.

| | No.1. | No.2. | No.3. |
|---|---|---|---|
| Chlorine | 23 | 40.32 | 39.5 |
| Lime | 46 | 45.40 | 39.9 |
| Water | 31 | 14.28 | 20.6 |
| | 100 | 100 | 100 |

The experiments of Dr Ure appear to have been made with great care, and his results to be entitled to equal if not greater confidence than those of the other chemists. Upon the whole it is probable, that common commercial bleaching powder consists of chloride of lime, a compound of 36 parts or one equivalent of chlorine, and 28 parts or one equivalent of lime; and that this, the essential ingredient, is mixed with variable quantities of hydrate of lime.

Several methods have been proposed for estimating the value of different specimens of the chloride of lime. Perhaps the most convenient for the artist is that of Welter, which consists in ascertaining the power of the bleaching liquid to deprive a solution of indigo of known strength of its colour; and directions have been drawn up by Gay-Lussac for enabling manufacturers to employ this method with accuracy. (Annals of Philosophy, xxiv. 218.) For analytical purposes, the best method is to decompose chloride of lime, confined in a glass tube over mercury, by means of muriatic acid. Muriate of lime is generated, and the chlorine being set free, its quantity may easily be measured.

The *protosulphuret of calcium* is procured by processes similar to those for forming the sulphuret of barium.

The phosphorescent substance called *Canton's phosphorus*, which is made by exposing a mixture of calcined oyster-shells and sulphur to a red heat, is supposed to be a sulphuret of lime; but its real composition has not been determined.

* Annals of Phil. i. 15. and ii. 6.
† Ibid. xv. 401.
‡ An. de Ch. et de Ph. vol. viii.
§ Quarterly Journ., xiii. 1.

*Phosphuret of Lime.*—This compound is formed by passing the vapour of phosphorus over fragments of quicklime at a red heat. The true nature of the product is not known with certainty. It is either a phosphuret of lime, or a mixture of phosphate of lime and phosphuret of calcium. When it is put into water, mutual decomposition ensues, and phosphuretted hydrogen, hypophosphorous acid, and phosphoric acid are generated. (Page 247.)

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## SECTION VII.

### *MAGNESIUM.*

The galvanic researches of Sir H. Davy have demonstrated the existence of magnesium, though he obtained it in a quantity too minute for determining its properties. He ascertained, however, that it decomposes water, and is converted by uniting with oxygen into magnesia.

Magnesia, the only known oxide of magnesium, is obtained by exposing carbonate of magnesia to a very strong red heat, by which its carbonic acid is expelled. It is a white friable powder, of an earthy appearance; and when pure, it has neither taste nor odour. Its specific gravity is about 2.3. It is exceedingly infusible. It has a weaker affinity than lime for water; for though it forms a hydrate when moistened, the combination is effected with hardly any disengagement of caloric, and the product is readily decomposed by a red heat. There probably exists several different compounds of water and magnesia, but the native hydrate is the only one known with certainty. According to the analysis of Stromeyer, this hydrate contains one equivalent of each of its constituents; and the results of the analysis of Berzelius and Dr Fyfe accord very nearly with this proportion.

Magnesia dissolves very sparingly in water. According to Dr Fyfe, it requires 5142 times its weight of water at 60°, and 36,000 of boiling water for solution. The resulting liquid does not change the colour of violets; but when pure magnesia is put upon moistened turmeric paper, it causes a brown stain. From this there is no doubt that the inaction of magnesia with respect to vegetable colours, when tried in the ordinary mode, is owing to its insolubility. It possesses the still more essential character of alkalinity, that, namely, of forming neutral salts with acids in an eminent degree. It absorbs both water and carbonic acid when exposed to the atmosphere, and therefore should be kept in well-closed phials.

The atomic weight of magnesia, as determined by Dr Thomson, is 20. Consequently this alkaline base, regarded as the protoxide of magnesium, is composed of

| | | | |
|---|---|---|---|
| Magnesium | . | 12 | or one proportional. |
| Oxygen | . | 8 | or one proportional. |

Magnesia is characterized by the following properties. With nitric and muriatic acids, it forms salts which are soluble in alcohol, and exceedingly deliquescent. The sulphate of magnesia is very soluble in water, a circumstance by which it is distinguished from the other alkaline earths. Magnesia is precipitated from its salts as a bulky hydrate by the pure alkalies. It is precipitated as carbonate of mag-

nesia, by the carbonates of potassa and soda; but the bicarbonates, and the common carbonate of ammonia, do not precipitate it in the cold. If moderately diluted, the salts of magnesia are not precipitated by oxalate of ammonia. By means of this reagent magnesia may be both distinguished and separated from lime.

The compounds of magnesium with the other simple substances have little interest. The chloride is formed by decomposing muriate of magnesia by heat; but it is apt to lose a portion of muriatic acid during the process. It is very deliquescent, and is soluble in alcohol. It is composed of 36 parts or one equivalent of chlorine, and 12 parts or one equivalent of magnesium.

# CLASS I.

## ORDER III.

### *METALLIC BASES OF THE EARTHS.*

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## SECTION VIII.

### *ALUMINIUM.*

That alumina is an oxidized body was proved by Sir H. Davy, who found that potassa is generated, when the vapour of potassium is brought into contact with pure alumina heated to whiteness; and it was inferred, chiefly by analogical reasoning, to be a metallic oxide. The propriety of this inference has been demonstrated by M. Wöhler, who has lately procured *aluminium*, the metallic base of alumina, in a pure state. (Edinburgh Journal of Science, No xvii. 178.)

The preparation of this metal depends on the property which potassium possesses, of decomposing the chloride of aluminium. Decomposition is effected by aid of a moderate increase of temperature; but the action is so violent, and accompanied with such intense disengagement of heat and light, that the process cannot be safely conducted in glass vessels. Dr Wöhler succeeded in effecting the decomposition in a platinum crucible, retaining the cover in its place by a piece of wire. The heat developed during the action was so great, that the crucible, though but gently heated externally, suddenly became red-hot. The platinum is scarcely attacked during the process; but to prevent the possibility of error from this source, the decomposition was effected in a crucible of porcelain. The potassium employed for the purpose should be quite free from carbon, and the quantity operated on at one time not exceed the size of ten peas. The heat was applied by means of a spirit lamp, and continued until the action was completed. The proportion of the materials requires to be carefully adjusted; for the potassium should be in such quantity as to prevent any chloride of aluminium from subliming during the process, but not so

much as to yield an alkaline solution when the product is put into water. The matter contained in the crucible at the close of the operation is in general completely fused, and of a dark gray colour. When *quite cold*, the crucible is put into a large glass full of water, in which the saline matter is dissolved, with slight disengagement of hydrogen of an offensive odour; and a gray powder separates, which on close inspection, especially in sunshine, is found to consist solely of minute scales of metal. After being well washed with *cold* water, it is pure aluminium. The solution is neutral, and contains a quantity of alumina, owing to a combination being formed between chloride of aluminium and chloride of potassium during the action.

Aluminium, as thus formed, is a gray powder, very similar to that of platinum. It is generally in small scales or spangles of a metallic lustre; and sometimes small, slightly coherent, spongy masses are observed, which in some places have the lustre and white colour of tin. The same appearance is rendered perfectly distinct by pressure on steel, or in an agate mortar; so that the lustre of aluminium is decidedly metallic. In its fused state it is a conductor of electricity, though it does not possess this property when in the form of powder. This remark, of a metal conducting the electric fluid in one state and not in another, is very instructive; and Dr Wöhler observed an instance of the same kind in iron, which in the state of fine powder is a non-conductor of electricity.

Aluminium requires for fusion a temperature higher than that at which cast iron is liquefied. When heated to redness in the open air, it takes fire and burns with vivid light, yielding aluminous earth of a white colour, and of considerable hardness. Sprinkled in powder in the flame of a candle, brilliant sparks are emitted, like those given off during the combustion of iron in oxygen gas. When heated to redness in a vessel of pure oxygen gas, it burns with an exceedingly vivid light, and emission of intense heat. The resulting alumina is partially vitrified, of a yellowish colour, and equal in hardness to the native crystallized aluminous earth, the corundum. Heated to near redness in an atmosphere of chlorine, it takes fire, and chloride of aluminium is sublimed.

Aluminium is not oxidized by water at common temperatures, nor is its lustre tarnished by lying in water during its evaporation. On heating the water to near its boiling point, oxidation of the metal commences, with feeble disengagement of hydrogen gas, the evolution of which continues even long after cooling, but at length wholly ceases. The oxidation, however, is very slight; and even after continued ebullition, the smallest particles of aluminium appear to have suffered scarcely any change.

Aluminium is not attacked by concentrated sulphuric or nitric acid at common temperatures. In the former, with the aid of heat, it is rapidly dissolved with disengagement of sulphurous acid gas. In dilute muriatic and sulphuric acid, it is dissolved with evolution of hydrogen gas. It is easily and completely dissolved even by a dilute solution of potassa, hydrogen gas being evolved at the same time. Ammonia produces a similar effect, and renders soluble a large quantity of aluminium. The hydrogen gas which makes its appearance is of course derived from water, the oxygen of which combines with aluminium.

Alumina is one of the most abundant productions of nature. It is found in every region of the globe, and in rocks of all ages, being a constituent of the oldest primary mountains, of the secondary strata, and of the most recent alluvial depositions. The different kinds of clay of

which bricks, pipes, and earthenware are made, consists of hydrate of alumina in a greater or less degree of purity. Though this earth commonly appears in rude amorphous masses, it is sometimes found beautifully crystallized. The ruby and the sapphire, two of the most beautiful gems with which we are acquainted, are composed almost solely of alumina.

Pure alumina is prepared from alum, the sulphate of alumina and potassa. The salt, as purchased in the shops, is frequently contaminated with oxide of iron, and consequently unfit for many chemical purposes; but it may be separated from this impurity by repeated crystallization. The absence of iron is proved by the alum being soluble without residue in a solution of pure potassa; whereas when oxide of iron is present, it is either left undissolved in the first instance, or deposited after a few hours in yellowish-brown flocks. Any quantity of purified alum is dissolved in four or five times its weight of boiling water, a slight excess of carbonate of potassa added, and after digesting for a few minutes, the bulky hydrate of alumina is collected on a filter, and well washed with hot water. It is necessary in this operation to digest, and employ an excess of alkali; since otherwise the precipitate would retain some sulphuric acid in the form of a sub-sulphate. But the alumina, as thus prepared, is not yet quite pure; for it retains some of the alkali with such force, that it cannot be separated by the action of water. For this reason the precipitate must be re-dissolved in dilute muriatic acid, and thrown down by means of pure ammonia or its carbonate. This precipitate, after being well washed and exposed to a white heat, yields pure anhydrous alumina. Ammonia cannot be employed for precipitating aluminous earth directly from alum, because the sulphate of alumina is not completely decomposed by this alkali. (Berzelius.) An easier process, proposed by Gay-Lussac, is to expose the sulphate of alumina and ammonia to a strong heat, so as to expel the ammonia and sulphuric acid.

Alumina has neither taste nor smell, and is quite insoluble in water. It is very infusible, though less so than lime or magnesia. It has a powerful affinity for water, attracting moisture from the atmosphere with avidity; and for a like reason, it adheres tenaciously to the tongue when applied to it. Mixed with a due proportion of water, it yields a soft cohesive mass, susceptible of being moulded into regular forms, a property upon which depends its employment in the art of pottery. When once moistened, it cannot be rendered anhydrous, except by exposure to a full white heat; and in proportion as it parts with water, its volume diminishes. (Page 41.)

Alumina most probably forms several different hydrates with water. Dr Thomson has described two different compounds of this kind. One is the bihydrate, composed of one equivalent of alumina to two of water; and it is procured by exposing, for the space of two months, alumina, precipitated by means of an alkali, to a dry air, the temperature of which does not exceed 60° F. The other compound is a protohydrate, obtained by drying the bihydrate at a temperature of 100° F. by which means half of its water is expelled.

Alumina, owing to its insolubility, does not affect the blue colour of plants. It appears to possess the properties both of an acid and of an alkali;—of an acid, by uniting with alkaline bases, such as potassa, lime, and baryta;—of an alkali, by forming salts with acids. In neither case, however, are its soluble compounds neutral with respect to test paper.

Chemists are not agreed as to the combining proportion of alumina;

but Dr Thomson, after comparing the results of a considerable number of analyses, has fixed upon 18 as its equivalent. The composition of alumina is still more uncertain, for as yet no direct experiment has been made on the subject. Dr Thomson considers it a compound of one proportional of aluminium and one of oxygen, and on this supposition, 10 is the equivalent of the former; but Berzelius believes its constitution to be analogous to that of the peroxide of iron, and a strong argument may be adduced in favour of this view.

Alumina is easily recognised by the following characters. 1. It is separated from acids, as a hydrate, by all the alkaline carbonates, and by pure ammonia. 2. It is precipitated by pure potassa or soda, but the precipitate is completely re-dissolved by an excess of the alkali.

*Chloride of Aluminium.*—This compound was discovered some years ago by Professor Oersted, by transmitting dry chlorine gas over a mixture of alumina and charcoal heated to redness. By acting on this substance with an amalgam of potassium and expelling the mercury by heat, he obtained metallic matter, which he believed to be aluminium; but not having leisure to pursue the inquiry himself, he requested Dr Wöhler to investigate the subject. Dr Wöhler did not arrive at any satisfactory conclusion by the method suggested by Oersted; but met with complete success by means of pure potassium, as already described.

To procure the chloride of aluminium, Dr Wöhler precipitated aluminous earth from a hot solution of alum by means of potassa, and mixed the hydrate, when dry, with pulverized charcoal, sugar, and oil, so as to form a thick paste, which was heated in a covered crucible, until all the organic matter was destroyed. By this means the alumina was brought into a state of intimate mixture with finely divided charcoal, and while yet hot, was introduced into a tube of porcelain, fixed in a convenient furnace. After expelling atmospheric air from the interior of the apparatus by a current of dry chlorine gas, the tube was brought to a red heat. The formation of chloride of aluminium then commenced, and continued, with disengagement of carbonic oxide gas, during an hour and a half, when the tube became impervious from sublimed chloride of aluminium collected within it. The process was then necessarily discontinued.

As thus formed, chloride of aluminium is of a pale greenish-yellow colour, partially translucent, and of a highly crystalline lamellated texture, somewhat like talc, but without regular crystals. On exposure to the air it fumes slightly, emits an odour of muriatic acid gas, and, deliquescing, yields a clear liquid. When thrown into water, it is speedily dissolved with a hissing noise; and so much heat is evolved that the water, if in small quantity, is brought into a state of brisk ebullition. The solution is the common muriate of alumina, formed by decomposition of water. According to Oersted, it is volatile at a temperature a little higher than 212°, and its point of fusion is nearly at the same degree.

*Sulphuret of Aluminium.*—Sulphur may be distilled from aluminium without combining with it; but if a piece of sulphur is dropped on aluminium when strongly incandescent, so that it may be enveloped in an atmosphere of the vapour of sulphur, the union is effected with vivid emission of light. The resulting sulphuret is a partially vitrified, semi-metallic mass, which acquires an iron-black metallic lustre when burnished. On exposure to the air, it emits a strong odour of sulphuretted hydrogen, swells up gradually, and falls into a gray powder, sulphuretted hydrogen gas and alumina being obviously generated at the expense of the watery vapour floating in the atmos-

phere. Applied to the tongue, it excites a pricking warm taste of sulphuretted hydrogen. When thrown into pure water, sulphuretted hydrogen gas is rapidly disengaged, and gray alumina deposited.

Dr Wöhler finds that sulphuret of aluminium cannot be generated by the action of hydrogen gas on sulphate of alumina at a red heat; for in that case all the acid is expelled, without the aluminous earth being reduced.

*Phosphuret of Aluminium.*—When aluminium is heated to redness in contact with the vapour of phosphorus, it takes fire, and emits a brilliant light. The product is described by Dr Wöhler as a blackish-gray pulverulent mass, which by friction acquires a dark gray metallic lustre, and in the air smells instantly of phosphuretted hydrogen. By the action of water, alumina and phosphuretted hydrogen gas are generated, but the latter is not spontaneously explosive. The effervescence is less rapid than with the sulphuret, but is increased by heat.

*Seleniuret of Aluminium.*—This compound is formed, with disengagement of heat and light, by heating to redness a mixture of selenium and aluminium. The product is black, pulverulent, and assumes a dark metallic lustre when rubbed. In the air, it emits a strong odour of seleniuretted hydrogen; and this gas is rapidly disengaged by the action of water, which is speedily reddened by the separation of selenium.

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## SECTION IX.

### *GLUCINIUM, YTTRIUM, ZIRCONIUM.*

### *Glucinium.*

*Glucina*, which was discovered by Vauquelin in the year 1798, has hitherto been found only in three rare minerals, the euclase, beryl, and emerald. It is supposed by analogy to be the oxide of a metal, and its supposed metallic base is called *Glucinium.**

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* Glucinium has been obtained in a separate state by Dr Wöhler: his process is as follows:—Mix pure glucina intimately with charcoal, and heat it to redness, exposed to a current of dry chlorine. A chloride of glucinium is thus obtained, sublimed in brilliant white needles, one part of which presents a compact texture, and the remainder a solid fused mass. Place the chloride thus formed in layers, in a platinum crucible, along with flattened pieces of potassium. Fix the cover on tightly by means of a wire, and heat with a spirit lamp. The reduction immediately takes place, and with so great an extrication of caloric, that the crucible becomes of a white-red heat. Allow the crucible to cool completely, take off the cover, and empty its contents into a large glass filled with water. The fused gray mass, consisting of the chlorides of potassium and glucinium, dissolves, while the glucinium remains behind in the form of a grayish-black powder, which is to be thrown upon a filter, washed and dried.

Glucinium is in the form of a dark gray powder, resembling in all respects a metal precipitated in the pulverulent form. Under the

Glucina is commonly prepared from beryl, in which it exists to the extent of about 14 per cent, combined with silica and alumina. In order to procure it in a separate state, the mineral is reduced to an exceedingly fine powder, mixed with three times its weight of carbonate of potassa, and exposed to a strong red heat for half an hour, so that the mixture may be fused. The mass is then dissolved in dilute muriatic acid, and the solution evaporated to perfect dryness; by which means the silica is rendered quite insoluble. The alumina and glucina are then redissolved in water acidulated with muriatic acid, and thrown down together with pure ammonia. The precipitate, after being well washed, is macerated with a large excess of carbonate of ammonia, by which glucina is dissolved; and on boiling the filtered liquid, carbonate of glucina subsides. By means of a red heat, the carbonic acid is entirely expelled.

Glucina is a white powder, which has neither taste nor odour, and is quite insoluble in water. Its specific gravity is 3. Vegetable colours are not affected by it. The salts which it forms with acids have a sweetish taste, a circumstance which distinguishes glucina from other earths, and from which its name is derived.* According to the analysis of Dr Thomson and Berzelius, 26 is the atomic weight of glucina.

Glucina may be known chemically by the following characters. 1. Pure potassa or soda precipitates glucina from its salts, but an excess of the alkali redissolves it. 2. It is precipitated permanently by pure ammonia as the hydrate, and by fixed alkaline carbonates, as carbonate of glucina. 3. It is dissolved completely by a cold solution of carbonate of ammonia, and is precipitated from it by boiling. By means of this property, glucina may be both distinguished and separated from alumina.

## *Yttrium.*

*Yttrium* † is the supposed metallic base of an earth which was discovered in the year 1794 by Professor Gadolin, in a mineral found at Ytterby in Sweden, from which it received the name of *Yttria*.

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burnisher, it assumes a dull metallic lustre. Its fusing point is very high. It undergoes no change either in air or when exposed to boiling water. When heated to redness on platinum foil, it takes fire, and burns with great brilliancy, and glucina is regenerated. In oxygen it burns with extraordinary brilliancy; and yet the glucina formed gives no indications of fusion. It burns also in chlorine, and in the vapours of bromine and iodine. *An. de Ch. et de Ph. Sep.* 1828. B.

* From γλυκὺς sweet.

† Yttrium was obtained by Dr Wöhler in the same manner as glucinium. (See note to the preceding page.) As first obtained, it presents the appearance of small scales, possessing a perfect metallic lustre. After being washed and dried, it appears under the form of a shining metallic powder, of a grayish-black colour. By reason of its metallic and crystalline appearance, it is readily distinguished from glucinium and aluminium. Under the burnisher, it gives a true metallic trace. It is very far, however, from having a metallic lustre comparable to that of aluminium, which is remarkably white and metallic. At ordinary temperatures, it is not oxidized either by air or water. Heated to redness in the open air, it takes fire and burns with dazzling splendour, regenerating yttria. In pure oxygen it burns with extraordinary brilliancy. *An. de Ch. et de Ph. Sep.* 1828. B.

Yttria resembles alumina and glucina in its chemical properties; but is distinguished from both by being insoluble in a solution of pure potassa. Its atomic weight, as deduced by Dr Thomson from the analyses of Berzelius, is 42.

The substance called *thorina*, supposed by Berzelius to be a distinct earth, has been recognised by that chemist to be phosphate of yttria*.

## *Zirconium.*

The experiments of Sir H. Davy proved zirconia to be an oxidized body, and afforded a presumption that its base, *zirconium*, is of a metallic nature. The decomposition of this earth, however, had not been effected in a satisfactory manner till the year 1824, when Berzelius succeeded in obtaining zirconium in an insulated state.

Zirconium is procured by heating a mixture of potassium, and hydrofluate of zirconia and potassa, carefully dried, in a tube of glass or iron, by means of a spirit lamp. The reduction takes place at a temperature below redness, and without emission of light. The mass is then washed with boiling water, and afterwards digested for some time in dilute muriatic acid. The residue is pure zirconium.

Zirconium, thus obtained, is in the form of a black powder, which may be boiled in water without being oxidized, and is attacked with difficulty by sulphuric, muriatic, or nitro-muriatic acid; but is dissolved readily, and with disengagement of hydrogen gas, by hydrofluoric acid. Heated in the open air it takes fire at a temperature far below luminousness, burns brightly, and is converted into zirconia. Its metallic nature seems somewhat questionable. It may indeed be pressed out into thin shining scales of a dark gray colour, and of a lustre which may be called metallic; but its particles cohere together very feebly, and it has not been procured in a state capable of conducting

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* Berzelius discovered in 1829 a new earth, to which he has given the name *thorina*, an appellation which he formerly applied to a substance, erroneously supposed by him to be an earth, but which he afterwards ascertained to be phosphate of yttria, as mentioned by Dr Turner.

Thorina is a constituent of a new mineral found at Brévig in Norway. It is white and irreducible by charcoal and potassium. Its specific gravity is 9.4. After having been strongly ignited, it is not attacked by any of the acids, except the concentrated sulphuric. It dissolves very readily in carbonate of ammonia. On heating the solution, a portion of the earth is precipitated, but is afterwards redissolved as the solution cools.

Thorinium, or the radical of thorina, is obtained by decomposing chloride of thorinium by means of potassium. It is a gray metallic powder, incapable of decomposing water, but which, when heated above redness, burns with a splendour nearly equal to that of the combustion of phosphorus in oxygen. It is but slightly acted on by nitric or sulphuric acid. Muriatic acid, on the contrary, dissolves it with brisk effervescence.

The sulphate of thorina has the remarkable property of being very soluble in cold water, but nearly insoluble in boiling water. The earth itself contains 11.8 per cent of oxygen; and assuming it to be a protoxide, the equivalent number of thorinium will be nearly 60. *An. de Ch. et de Ph. Août* 1829. B.

electricity. These points, however, require further investigation before a decisive opinion on the subject can be adopted*.

Zirconia was discovered in the year 1789 by Klaproth in the Jargon or Zircon of Ceylon, and has since been found in the Hyacinth from Expailly in France. It is an earthy substance, resembling alumina in appearance, of specific gravity 4.3, having neither taste nor odour, and quite insoluble in water. Its colour, when pure, is white; but it has frequently a tinge of yellow, owing to the presence of iron, from which it is separated with great difficulty. Its salts are distinguished from those of alumina or glucina by being precipitated by all the pure alkalies, in an excess of which it is insoluble. The alkaline carbonates precipitate it as carbonate of zirconia, and a small portion of it is redissolved by an excess of the precipitant.

The composition of zirconia has not yet been satisfactorily determined. From some analyses by Berzelius, described in the Essay above referred to, it is probable that the atomic weight of this earth is about 30 or 33.

*Sulphuret of Zirconium.*—This compound may be prepared, according to Berzelius, by heating zirconium with sulphur in an atmosphere of hydrogen gas; and the union is effected with feeble emission of light. The product is pulverulent, a non-conductor of electricity, of a dark chesnut-brown colour, and without lustre. It is insoluble in sulphuric, nitric, and muriatic acid; and it is slowly attacked by nitro-muriatic acid, even with the aid of heat. It is readily dissolved by hydrofluoric acid, with disengagement of hydrogen gas.

## SECTION X.

### *SILICIUM.*

That silica or siliceous earth is composed of a combustible body united with oxygen, was demonstrated by Sir H. Davy; for on bringing the vapour of potassium in contact with pure silica heated to whiteness, a compound of silica and potassa resulted, through which was diffused the inflammable base of silica, in the form of black particles like plumbago. To this substance, on the supposition of its being a metal, the term *silicium* was applied. But though this view has been adopted by most chemists, so little was known with certainty concerning the real nature of the base of silica, that Dr Thomson inclined to the opinion of its being a non-metallic body, and accordingly associated it, in his system of chemistry, with carbon and boron under the name of *silicon*. The recent researches of Berzelius appear almost decisive of this question. A substance which wants the metallic lustre, and is a non-conductor of electricity, cannot be regarded as a metal. It may not be improper, however, to have the absence of these qualities more completely ascertained, before separating silica from a class of bodies with which, in several respects, it is so nearly allied.

Pure silicium was first procured by Berzelius in the year 1824 by

* Poggendorff's Annalen, vol. iv., or Quarterly Journal of Science, xviii. 157.

the action of potassium on fluosilicic acid gas; but it is more conveniently prepared from the double hydrofluate of silica and potassa or soda, previously dried by a temperature near that of redness. In this state the compound may be regarded as a double fluoride, in which neither oxygen nor hydrogen are present; and when heated in a glass tube with potassium, this metal unites with fluorine, and silicium is separated. The heat of a spirit lamp is sufficient for the purpose, and the decomposition takes place, accompanied with feeble detonation, before the mixture becomes red-hot. When the mass is cold, the soluble parts are removed by the action of water; the first portions of which produce disengagement of hydrogen gas, owing to the presence of some siliciuret of potassium. The silicium thus procured is chemically united with a little hydrogen, and at a red heat burns vividly in oxygen gas. In order to render it quite pure, it should be first heated to redness, and then digested in dilute hydrofluoric acid to dissolve adherent particles of silica. (Annals of Philosophy, xxvi. 116.)

Silicium, obtained in this manner, has a dark nut-brown colour, without the least trace of metallic lustre. It is a non-conductor of electricity. It is incombustible in air and in oxygen gas; and may be exposed to the flame of the blowpipe without fusing or undergoing any other change. It is neither dissolved nor oxidixed by the sulphuric, nitric, muriatic, or hydrofluoric acid; but a mixture of the nitric and hydrofluoric acids dissolves it readily even in the cold*.

Silicium is not changed by ignition with chlorate of potassa. In nitre it does not deflagrate, until the temperature is raised so high that the acid is decomposed; and then the oxidation is effected by the affinity of the disengaged alkali for silica, cooperating with the attraction of oxygen for silicium. For a similar reason it burns vividly

* Dr Turner has not, I think, described in a sufficiently distinct manner the two states under which silicium appears. Its characters are so much altered by exposure to a high temperature, that Berzelius has deemed it expedient to give a separate description of the properties which it presents before and after ignition.

Silicium before ignition is neither dissolved nor oxidized by sulphuric, nitric, or nitro-muriatic acid, even at the boiling temperature; but is soluble in liquid hydrofluoric acid† at common temperatures, and in a heated concentrated solution of caustic potassa. It burns readily and vividly in air, and still more vividly in oxygen gas. A part of it only undergoes combustion, the remainder being protected by the coating of silica which becomes formed. In this state silicium contains a little hydrogen.

If a portion of silicium which has undergone combustion on its surface, be subjected to the action of hydrofluoric acid, the silica is removed, and a nucleus of silicium is obtained in that state in which it exists, after having been condensed and altered in its properties by heat. It is now perfectly incombustible, and is no longer soluble in hydrofluoric acid or a solution of caustic potassa.

Berzelius does not appear to attribute the difference in properties of the two varieties of silicium to the presence of hydrogen in one of them; but rather to a difference in the aggregation of the particles. *Berzelius, Traité de Chimie, I.* 370. B.

† The acid given in the French edition of Berzelius's work is the *hydrochloric;* but this is evidently a mistake. B.

when brought into contact with carbonate of potassa or soda, and the combustion ensues at a temperature considerably below redness. It explodes, in consequence of a copious evolution of hydrogen gas, when it is dropped upon the fused hydrate of potassa, soda, or baryta.

## *Oxide of Silicium, or Silica.*

Silica exists in the earth in great quantity. It enters into the composition of most of the earthy minerals; and under the name of quartz rock, forms independent mountainous masses. It is the chief ingredient in sandstones; and flint, calcedony, rock crystal, and other analogous substances, consist almost entirely of silica. Siliceous earth of sufficient purity for most purposes may, indeed, be procured by igniting transparent specimens of rock crystal, throwing them while red-hot into water, and then reducing them to powder.

Pure silica, in this state, is a light white powder, which feels rough and dry when rubbed between the fingers, and is both insipid and inodorous. It is fixed in the fire, and is very infusible; but fuses before the oxy-hydrogen blowpipe with greater facility than lime or magnesia.

In its solid form, it is quite insoluble in water; but Berzelius has shown that, when silica in the nascent state is in contact with that fluid, it is dissolved in large quantity. On evaporating the solution gently, a bulky gelatinous substance separates, which is the hydrate of silica. This hydrate is partially decomposed by a very moderate temperature; but a red heat is required for expelling the whole of the water. According to Dr Thomson, silica unites with water in several proportions. (First Principles, vol. i. p. 191.)

Silica, most likely from its insolubility, does not change the blue vegetable colours. It appears to possess the properties of an acid rather than of an alkali. Thus, no acid acts upon silica except the hydrofluoric acid; whereas it is dissolved by solutions of the fixed alkalies, and combines with many of the metallic oxides. On this account silica is termed *silicic acid* by some chemists, and its compounds with alkaline bases *silicates*. The compound earthy minerals that contain silica may be regarded as native silicates.

The combination of silica with the fixed alkalies is best effected by mixing pure sand with carbonate of potassa or soda, and heating the mixture to redness. During the process, carbonic acid is expelled, and a silicate of the alkali is generated. The nature of the product depends upon the proportions which are employed. On igniting one part of silica with three of the carbonate of potassa, a vitreous mass is formed, which is deliquescent, and may be dissolved completely in water. This solution, which was formerly called *liquor silicum*, has an alkaline reaction, and absorbs carbonic acid on exposure to the atmosphere, by which it is partially decomposed. Concentrated acids precipitate the silica as a gelatinous hydrate; but if a considerable quantity of water is present, and the acid is added gradually, the alkali may be perfectly neutralized without any separation of silica. When a solution of this kind is evaporated to dryness, the silica is rendered quite insoluble, and may thus be obtained in a pure form.

But if the proportion of silica and alkali is reversed, a transparent brittle compound results, which is insoluble in water, is attacked by none of the acids excepting the hydrofluoric, and possesses the well-known properties of glass. Every kind of glass is composed of silica

and an alkali, and all its varieties are owing either to differences in the proportions of the constituents, to the nature of the alkali, or to the presence of foreign matters. Thus the green bottle glass is made of impure materials, such as river sand, which contains iron, and the most common kind of kelp or pearlashes. Crown glass for windows is made of a purer alkali, and sand which is free from iron. Plate glass, for looking-glasses, is composed of sand and alkali in their purest state; and in the formation of flint glass, besides these pure ingredients, a considerable quantity of litharge or red lead is employed. A small portion of the peroxide of manganese is also used, in order to oxidize carbonaceous matters contained in the materials of the glass; and nitre is sometimes added with the same intention.

Berzelius ascertained the composition of silica by oxidizing a known quantity of silicium, and weighing the product carefully; and according to this synthetic experiment, 100 parts of silica are composed of 48 parts of silicium and 52 parts of oxygen. The atomic weight of silica, deduced apparently with great care by Dr Thomson, is precisely 16. Chemists are not agreed about the atomic constitution of silica. Berzelius considers it a compound of one atom of silicium and three atoms of oxygen; but the opinion of Dr Thomson, that it is composed of an atom of each element, is both more simple and agrees better with the combining proportion of silica. According to this view, and adopting 16 as the equivalent of silica, 8 is of course the equivalent of silicium, an inference which accords very nearly with the experimental result of Berzelius.

*Chloride of Silicium.*—When silicium is heated in a current of chlorine gas, it takes fire, and is rapidly volatilized. The product of the combustion condenses into a liquid, which appears to be naturally colourless, but to which an excess of chlorine communicates a yellow tint. This fluid is very limpid and volatile, and evaporates almost instantaneously in open vessels in the form of a white vapour. It has a suffocating odour not unlike that of cyanogen, and when put into water is converted into muratic acid and silica, the latter being easily obtained in the gelatinous form. (Berzelius.)

*Sulphuret of Silicium.*—This compound is formed by heating silicium in the vapour of sulphur, and the union is attended with the phenomena of combustion. The product is a white earthy looking substance, which is instantly converted by the action of water into sulphuretted hydrogen and silica; and while the former escapes with effervescence, the latter is dissolved in large quantity. In open vessels, owing to the moisture of the atmosphere, it undergoes a similar change; but in dry air it may be kept unaltered.

## *Fluosilicic Acid Gas.*

This gas is formed whenever hydrofluoric acid comes in contact with siliceous earth; and this is the reason why pure hydrofluoric acid can be prepared in metallic vessels only, and with fluor spar that is free from rock crystal. The most convenient method of procuring the gas is to mix in a retort one part of pulverized fluor spar with its own weight of sand or pounded glass, and two parts of strong sulphuric acid. On applying a gentle heat, fluosilicic acid gas is disengaged with effervescence, and may be collected over mercury.

The chemical changes attending the process are differently explained, according to the view which is taken concerning the nature of the product. In regarding fluor spar as a compound of fluoric acid and

lime, the former, at the moment of being set free, is thought to unite directly with silica; so that the resulting compound consists of silica and fluoric acid. But for reasons already stated, (page 226) fluor spar is here not considered as a fluate of lime; and therefore this view cannot be admitted. It is inferred, on the contrary, that when, by the action of sulphuric acid on fluoride of calcium, hydrofluoric acid is generated, the elements of this acid react on those of silica, and give rise to the production of water and fluosilicic acid gas. This gas is, therefore, a fluoride of silicium; and though in compliance with the usage of other chemist, I have retained its ordinary name, its title to be considered an acid is questionable. It may occur to some whether hydrofluoric acid does not unite directly with silica; but this idea is inconsistent with the proportion in which the elements of the gas are found to be united.

This compound is a colourless gas, which extinguishes flame, destroys animals that are immersed in it, and irritates the respiratory organs powerfully. It does not corrode glass vessels provided they are quite dry. When mixed with atmospheric air, it forms a white cloud, owing to the presence of watery vapour. Its specific gravity, according to Dr Thomson, is 3.6111; and 100 cubic inches of it, at 60° F. and when the barometer stands at 30 inches, weigh 110.138 grains.

Water acts powerfully on fluosilicic acid gas, of which it condenses, according to Dr John Davy, 365 times its volume. (Philos. Trans. for 1812.) The gas suffers decomposition at the moment of contact with water, depositing part of its silica in the form of a gelatinous hydrate, which when well washed is pure. The liquid, which has a sour taste and reddens litmus paper, contains the whole of the hydrofluoric acid, together with two-thirds of the silica which was originally present in the gas. (Berzelius.) By conducting the fluosilicic acid gas into a solution of ammonia, complete decomposition ensues:—hydrofluoric acid unites with the alkali, forming hydrofluate of ammonia, and all the silica is deposited. On this fact is founded the mode of analyzing fluosilicic acid gas, adopted by Dr Davy and Dr Thomson. According to the results obtained by Thomson, which appear more correct than those of Dr Davy, this gas is composed of 18.86 parts or one equivalent of fluorine, and 8 parts or one equivalent of silicium. Considered as a compound of fluoric acid and silica, it consists of 10.86 parts or one equivalent of fluoric acid, and 16 parts or one equivalent of silica.

The solution which is formed by fully saturating water with fluosilicic acid gas is powerfully acid, and emits fumes on exposure to the air. It is commonly known by the name of *silicated fluoric acid;* but a more appropriate term is *silico-hydrofluoric acid*. According to the experiments of Berzelius, it appears to be a definite compound of hydrofluoric acid and silica, in the ratio of three equivalents of the former to two of the latter. If evaporated before separation from the silica deposited by the action of water on fluosilicic acid gas, this compound is reproduced. But if the solution is poured off from the silica thus deposited, and then evaporated, fluosilicic acid gas is at first evolved, and subsequently hydrofluoric acid and water are expelled. The evaporation of silico-hydrofluoric acid *in vacuo* is attended by a similar change, so that this acid cannot be obtained free from water. It does not corrode glass; but when evaporated in glass vessels, the production of free hydrofluoric acid of course gives rise to corrosion.

On neutralizing silico-hydrofluoric acid with ammonia, and gently

evaporating to dryness, all the silica is rendered insoluble. By exactly neutralizing with carbonate of potassa, nearly all the silica and acid are precipitated in the form of a sparingly soluble double hydrofluate of silica and potassa; and a still more complete precipitation is effected by muriate of baryta in excess, when hydrofluate of silica and baryta is generated. A variety of similar compounds may be obtained either by double decomposition, or by the action of silico-hydrofluoric acid on metallic oxides. Most of these salts are soluble in water, those of potassa, soda, lime, baryta, and yttria, being the only sparingly soluble ones noticed by Berzelius. They have in general a sour bitter taste, redden litmus paper, and are decomposed at a high temperature with disengagement of fluosilicic acid gas. These salts were formerly known by the name of *fluosilicates*, in which silica and fluoric acid were thought to act the part of a compound acid; but Berzelius has shown that this view is inaccurate, and that they may be regarded as double salts, consisting of two proportionals of hydrofluate of silica, and one proportional of a hydrofluate of some other base.

Most of the facts contained in the preceding account of silico-hydrofluoric acid are drawn in part from an Essay of Berzelius in the Annals of Philosophy, xxiv. 450, but chiefly from his *Lehrbuch der Chemie*, i. 631.

# CLASS II.

## METALS, THE OXIDES OF WHICH ARE NEITHER ALKALIES NOR EARTHS.

## ORDER I.

### *METALS WHICH DECOMPOSE WATER AT A RED HEAT.*

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## SECTION XI.

### *MANGANESE.*

Manganese, which was discovered in the year 1774 by Gahn and Scheele, is a hard brittle metal, of a grayish-white colour, and granular texture. Its specific gravity is 6.85. When pure it is not attracted by the magnet. It is exceedingly infusible, requiring a heat of 160° Wedgwood for fusion. It soon tarnishes on exposure to the air, and absorbs oxygen with rapidity when heated to redness in open vessels. It is said to decompose water at common temperatures with disengagement of hydrogen gas, though the process is exceedingly slow; but at a red heat decomposition is rapid, and protoxide of man-

ganese is generated. The decomposition of water is likewise occasioned by dilute muriatic or sulphuric acid, and the muriate or sulphate of the protoxide of manganese is the product.

Manganese, owing doubtless to its powerful affinity for oxygen, has never been found in an uncombined state in the earth; but the peroxide of manganese occurs abundantly. This metal retains its oxygen with such force that its oxides require a stronger heat for reduction than potassa or soda. The method by which Gahn succeeded in procuring metallic manganese, was by exposing the peroxide, surrounded with charcoal, to the most intense heat of a smith's forge; and this process has been successfully repeated by others. (Berthier in An. de Ch. et de Ph. vol. xx.)

## *Oxides of Manganese.*

Different opinions have prevailed concerning the number of the oxides of manganèse; nor do chemists, even at present, seem quite decided upon the subject. The existence, however, of four distinct compounds, containing manganese and oxygen, may be regarded as certain. One of these, called the red oxide, is obviously composed of two of the others; so that the number of the real oxides of manganese does not exceed three. Their composition has been particularly investigated by Dr Thomson*, M. Arfwedson†, M. Berthier‡, and very lately by myself§. I am satisfied that the results obtained by Dr Thomson and myself are very near the truth, and they agree closely with those of the two others. Accordingly, the composition of these oxides may be thus stated.—

| | *Manganese.* | *Oxygen.* |
|---|---|---|
| Protoxide | 28, or one equivalent, | 8, or one equivalent. |
| Deutoxide | 28 . . | 12, or one and a half equivalents. |
| Peroxide | 28 . . | 16, or two equivalents. |

*Peroxide.*—This is the well-known ore commonly called from its colour the black oxide of manganese, the nature of which was ascertained in 1774 by Scheele. It generally occurs massive, of an earthy appearance, and mixed with other substances, such as siliceous and aluminous earths, oxide of iron, and carbonate of lime. It is sometimes found, on the contrary, in the form of minute prisms grouped together, and radiating from a common centre. This oxide may be made artificially by exposing the nitrate of manganese to a commencing red heat, until the whole of the nitric acid is expelled; but I have never succeeded in procuring it quite pure by this process, because the heat required to drive off the last traces of acid, likewise expel some oxygen from the peroxide.

Peroxide of manganese undergoes no change on exposure to the air. It is insoluble in water, and does not unite either with acids or alkalies. When boiled with sulphuric acid, it yields oxygen gas, and a sulphate of the protoxide is formed. (Page 134.) With muriatic acid, a muriate of the protoxide is generated, and chlorine is evolved.

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* First Principles, vol. i.

† Letter from Berzelius in the Annales de Ch. et de Ph. vol. vi.

‡ Ibid. xx.

§ Philos. Trans. of Edinburgh for 1828; or Philosophical Magazine and Annals for July, 1828.

(Page 196.) The solution in both cases is of a deep red colour, provided any undissolved oxide is present; but if separated from the undissolved portions, it is readily rendered colourless by heat. The action of sulphuric acid in the cold is exceedingly tardy and feeble, a minute quantity of oxygen gas is slowly disengaged, and the acid acquires an amethyst-red tint. On exposure to a red heat, it is converted, with evolution of oxygen gas, into the deutoxide of manganese. (Page 135.)

Peroxide of manganese is employed in the arts in the manufacture of glass, and in preparing chlorine for bleaching. In the laboratory, it is used for procuring chlorine and oxygen gases, and in the preparation of the salts of manganese.

*Deutoxide.*—This oxide occurs nearly pure in nature, and as a hydrate it is found abundantly, often in large prismatic crystals, at Jhlefeld in the Hartz. It may be formed artificially by exposing peroxide of manganese for a considerable time to a moderate red heat, and, therefore, is the chief residue of the usual process for procuring a supply of oxygen gas; but it is difficult so to regulate the degree and duration of the heat, that the resulting oxide shall be quite pure.

The colour of the deutoxide of manganèse varies with the source from which it is derived. That which is procured by means of heat from the native peroxide or hydrated deutoxide, has a brown tint; but when prepared from nitrate of manganese, it is nearly as black as the peroxide, and the native deutoxide is of the same colour. With sulphuric and muriatic acids, it gives rise to the same phenomena as the peroxide; but of course yields a smaller proportional quantity of oxygen and chlorine gases. It is more easily attacked than the peroxide by cold sulphuric acid. With strong nitric acid, it yields a soluble protonitrate and the peroxide, as observed by Berthier; and when boiled with dilute sulphuric acid, it undergoes a similar change. From the proportion of oxygen and manganese in this oxide, it may be regarded as a compound of 44 parts or one equivalent of the peroxide, and 36 parts or one equivalent of the protoxide of manganese.

*Protoxide.*—By this term is meant that oxide of manganese which is a strong salifiable base, is contained in all the ordinary salts of this metal, and which appears to be its lowest degree of oxidation. This oxide may be formed, as was shown by Berthier, by exposing the peroxide, deutoxide, or red oxide of manganese to the combined agency of charcoal and a white heat; and Dr Forchhammer, in the Annals of Philosophy, xvii. 52, has described an elegant mode of preparation, by exposing either of the oxides of manganese contained in a tube of glass, porcelain, or iron, to a current of hydrogen gas at an elevated temperature. The best material for this purpose is the red oxide prepared from nitrate of manganese; for some of the oxides, especially the peroxide, are fully reduced to the state of protoxide by hydrogen with difficulty. The reduction commences at a low red heat; but to decompose all the red oxide, a full red heat is required. The same compound is formed by the action of hydrogen gas at an intense white heat.

Protoxide of manganese, when pure, is of a pretty light green colour, very near the mountain-green. According to Forchhammer, it attracts oxygen rapidly from the air; but in my experiments, it was very permanent, undergoing no change either in weight or appearance during the space of nineteen days. At 600° F. it is oxidized with considerable rapidity, and at a low red heat is converted in an instant into the red oxide. According to Forchhammer and Arfwedson, it

takes fire when thus heated; but I have never observed this phenomenon. It unites readily with acids without effervescence, producing the same salts as when the same acids act on carbonate of manganese. When it comes in contact with concentrated sulphuric acid, intense heat is instantly evolved; and the same phenomenon is produced, though in a less degree, by strong muriatic acid. The resulting salt is the same as when these acids are heated with either of the other oxides of manganese. If quite pure, the protoxide should readily and completely dissolve in cold dilute sulphuric acid, and yield a colourless solution.

In order to prepare a pure salt of manganese from the common peroxide of commerce, either of the following processes should be employed. The impure deutoxide left in the process for procuring oxygen gas from the peroxide by means of heat, is mixed with a sixth of its weight of charcoal in powder, and exposed to a white heat for half an hour in a covered crucible. The protoxide thus formed is to be dissolved in muriatic acid, the solution evaporated to dryness, and the residue kept for a quarter of an hour in perfect fusion; being protected as much as possible from the air. By this means the chlorides of iron, calcium, and other metals are decomposed. The fused chloride of manganese is then poured out on a clean sandstone, dissolved in water, and the solution separated from insoluble matters by filtration. If free from iron, it will give a white precipitate with ferrocyanate of potassa, without any appearance of green or blue, and a flesh-coloured precipitate with hydrosulphuret of ammonia. The absence of lime may be proved, or traces of it separated, by oxalate of potassa. The manganese is then thrown down as a white carbonate by the bicarbonate of potassa or soda; and from this salt, after being well washed, all the other salts of manganese may be prepared. The other method of forming a pure muriate was suggested by Mr Faraday, and consists of heating to redness a mixture of peroxide of manganese with half its weight of muriate of ammonia. Owing to the volatility of the sal ammoniac, it is necessary to apply the required heat as rapidly as possible, and this is best done by projecting the mixture in small portions at a time into a crucible kept red-hot. In this process, the chlorine of the muriatic acid unites with the metal of the oxide to the exclusion of every other substance, provided an excess of manganese be present. The resulting chloride is then dissolved in water, and the insoluble matters separated by filtration. (Faraday in Quarterly Journal, vol. vi.)

The salts of manganese are in general colourless if quite pure; but more frequently they have a shade of pink, owing to the presence of a little red oxide. The protoxide is precipitated from their solutions, as the white hydrate by ammonia, or the pure fixed alkalies; as the white carbonate of manganese by alkaline carbonates and bicarbonates; as the white ferrocyanate of manganese by ferrocyanate of potassa, a character by which the absence of iron may be demonstrated. These white precipitates, with the exception of that obtained by means of a bicarbonate, very soon become brown from the absorption of oxygen. None of the salts of manganese which contain a strong acid, such as the nitric, muriatic, or sulphuric acid, are precipitated by sulphuretted hydrogen. With an alkaline hydrosulphuret, on the contrary, a flesh-coloured precipitate is formed, which is either a hydrosulphuret of the protoxide, or a hydrated protosulphuret of metallic manganese. When heated in close vessels, it yields a dark coloured sulphuret, and water is evolved.

*Red Oxide.*—The substance called red oxide of manganese, the

*oxidum manganoso-manganicum* of Arfwedson, occurs as a natural production, and may be formed artificially by exposing the peroxide or deutoxide to a white heat, either in close or open vessels. It is also produced by absorption of oxygen from the atmosphere, when the protoxide is precipitated from its salts by pure alkalies, or when the anhydrous protoxide or carbonate is heated to redness. It is very permanent in the air, not passing to a higher stage of oxidation at any temperature. Its colour when rubbed to the same degree of fineness is brownish-red when cold, and nearly black while warm. Fused with borax or glass, it communicates a beautiful violet tint, a character by which manganese may be easily detected before the blowpipe; and it is the cause of the rich colour of the amethyst. It is acted on by strong sulphuric and muriatic acids, with the aid of heat, in the same manner as the peroxide and deutoxide, but of course yields proportionally a smaller quantity of oxygen and chlorine gases. By cold concentrated sulphuric acid, it is dissolved in small quantity, without appreciable disengagement of oxygen gas, and the solution is promoted by a slight increase of temperature. The liquid has an amethyst tint, which disappears when heat is applied, or by the action of deoxidizing substances, such as protomuriate of tin, or nitrous, sulphurous, and phosphorous acids, protosulphate of manganese being generated. The pink colour which the salts of manganese generally possess, is owing to the presence of a small quantity of red oxide. By strong nitric acid, or when boiled with dilute sulphuric acid, it undergoes the same kind of change as the deutoxide.

The red oxide of manganese contains more oxygen than the protoxide and less than the deutoxide. Its elements are in such proportion, that it may be regarded as a compound either of

$$\left.\begin{array}{ll}\text{Deutoxide} & 80 \text{ or two equiv.}\\ \text{Protoxide} & 36 \text{ or one equiv.}\end{array}\right\} \text{ or } \left\{\begin{array}{ll}\text{Peroxide} & 44 \text{ or one equiv.}\\ \text{Protoxide} & 72 \text{ or two equiv.}\end{array}\right.$$

$$\begin{array}{ccc}\overline{116} & \qquad\qquad & \overline{116}\end{array}$$

It contains 27.586 per cent of oxygen, and loses 6.896 per cent of oxygen, when converted into the green oxide.

It has been inferred from some experiments of Berzelius and John, that there are two other oxides of manganese, which contain less oxygen than the green or protoxide. We have no proof, however, of the existence of such compounds.

Manganese is one of those metals which is capable of forming an acid with oxygen. When the peroxide of manganese is mixed with an equal weight of nitre or carbonate of potassa, and the mixture is exposed to a red heat, a green-coloured fused mass is formed, which has been long known under the name of *mineral chameleon*. On putting this substance into water, a green solution is obtained, the colour of which soon passes into blue, purple, and red; and ultimately, a brown flocculent matter, the red oxide of manganese, subsides, and the liquid becomes colourless. These changes take place more rapidly by dilution, or by employing hot water. We are indebted to MM. Chevillot and Edwards for a consistent explanation of these phenomena*. They demonstrated that the peroxide of manganese, when fused with potassa, absorbs oxygen from the atmosphere, and is thereby converted into an acid, the *manganesic*, which unites with the alkali. They attributed the different changes of colour above mentioned to

* An. de Ch. et de Ph. vol. viii.

the combination of this acid with different proportions of potassa. By evaporating the red solution rapidly, they succeeded in obtaining a manganesiate of potassa in the form of small prismatic crystals of a purple colour. This salt yields oxygen to combustible substances with great facility, and detonates powerfully with phosphorus. It is decomposed when in solution by very slight causes, being converted into the red oxide of manganese.

The subsequent researches of Dr Forchhammer render it probable that the green and red colours are produced by two distinct acids, the *manganeseous* and manganesic, the former giving rise to the green, and the latter to the red tint. He succeeded in forming a solution of manganesic acid in the following manner. A mixture of the nitrate of baryta was heated with peroxide of manganese, by which means the manganesite of baryta was generated; and to this salt, after having been well washed with water, a quantity of dilute sulphuric acid was added, precisely sufficient for combining with its base. The manganeseous acid, at the moment of being set free, resolved itself into the deutoxide of manganese and manganesic acid, and the latter, dissolving in the water, formed a beautiful red solution. Dr Forchhammer infers from his analysis of these compounds, that the manganeseous acid contains three and the manganesic four atoms of oxygen united with one atom of manganese. (Annals of Philosophy, vol. xvi.)

*Chloride of Manganese.*—This compound is best prepared by evaporating a solution of muriate of manganese to dryness by a gentle heat, and heating the residue to redness in a glass tube, while a current of muriatic acid gas is transmitted through it. The heat of a spirit lamp is sufficient for the purpose. It fuses readily at a red heat, and forms a pink-coloured lamellated mass on cooling. It is deliquescent, and of course very soluble in water, being converted by that fluid, with evolution of caloric, into muriate of manganese. It is composed of 28 parts or one equivalent of manganese, and 36 parts or one equivalent of chlorine.

A new chloride of manganese, remarkable for its volatility, has lately been described by M. Dumas. (Edinburgh Journal of Science, No. xv. 179.) It is readily formed by putting a solution of manganesic into strong sulphuric acid, and then adding fused sea-salt. The muriatic and manganesic acids mutually decompose each other; water and perchloride of manganese are generated, and the latter escapes in the form of vapour. The best mode of preparation is to form the common green mineral chameleon, and convert it into red by means of sulphuric acid. The solution, when evaporated, leaves a residue of sulphate and manganesiate of potassa. This mixture, treated by strong sulphuric acid, yields a solution of manganesic acid, into which are added small fragments of sea-salt, as long as coloured vapour continues to be evolved.

The new chloride, when first formed, appears as a vapour of a copper or greenish colour; but on traversing a glass tube cooled to 5° or −4° F, it is condensed into a greenish-brown coloured liquid. When generated in a capacious tube, its vapour gradually displaces the air, and soon fills the tube. If it is then poured into a large flask, the sides of which are moist, the colour of the vapour changes instantly on coming into contact with the moisture, a dense smoke of a pretty rose tint appears, and muriatic and manganesic acids are generated. From this it is manifest, that the new chloride is proportional to manganesic acid; that is, when its chlorine unites with hydrogen, the oxygen required to constitute water with that hydrogen exactly suffices for forming manganesic acid with the manganese. It is hence

supposed to consist of 28 parts or one equivalent of manganese, and 144 parts or four equivalents of chlorine.

*Fluoride of Manganese.*—A gaseous compound of fluorine and manganese has been lately discovered by M. Dumas and Dr Wöhler. (Edinburgh Journal of Science, No. xviii.) It is best formed by mixing common mineral chameleon with half its weight of fluor spar, and decomposing the mixture in a platinum vessel by fuming sulphuric acid. The fluoride is then disengaged in the form of a greenish-yellow gas or vapour, of a more intensely yellow tint than chlorine. When mixed with atmospheric air, it instantly acquires a beautiful purple-red colour; and is freely absorbed by water, yielding a solution of the same red tint. It acts instantly on glass, with formation of fluosilicic acid gas, a brown matter being at the same time deposited, which becomes of a deep purple-red tint on the addition of water.

From the experiments of Dr Wöhler, this yellow gas may be inferred to be a fluoride of manganese; that when mixed with water both compounds are decomposed, and hydrofluoric and manganesic acids generated, which are dissolved; that a similar formation of the two acids ensues from the admixture of the yellow gas with atmospheric air, owing to the moisture contained in the latter; and that by contact with glass, fluo-silicic acid gas is produced, and anhydrous manganesic acid deposited. In consequence of its acting so powerfully on glass, its other properties have not been ascertained; but from those above mentioned, its composition is obviously similar to that of the gaseous chloride of manganese. It hence consists of one equivalent of manganese, and four equivalents of fluorine.

The *protosulphuret of manganese* may be procured by igniting the sulphate with one-sixth of its weight of charcoal in powder. (Berthier.) It is also formed by the action of sulphuretted hydrogen on the protosulphate at a red heat. (Arfwedson in An. of Phil. vol. vii. N. S.) It occurs native in Cornwall and at Nagyag in Transylvania. It dissolves completely in dilute sulphuric or muriatic acid, with disengagement of very pure sulphuretted hydrogen gas.

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## SECTION XII.

### *IRON.*

Iron has a peculiar gray colour, and strong metallic lustre, which is susceptible of being heightened by polishing. In ductility and malleability, it is inferior to several metals, but exceeds them all in tenacity. (Page 266.) At common temperatures, it is very hard and unyielding, and its hardness may be increased by being heated and then suddenly cooled; but it is at the same time rendered brittle. When heated to redness, it is remarkably soft and pliable, so that it may be beaten into any form, or be intimately incorporated or *welded* with another piece of red-hot iron by hammering. Its texture is fibrous, and its specific gravity 7.78. In its pure state, it is exceedingly infusible, requiring for fusion a temperature of 158° of Wedgwood's pyrometer. It is attracted by the magnet, and may itself be rendered permanently magnetic by several processes;—a property of great interest and importance, and which is possessed by no other metal excepting cobalt and nickel.

The occurrence of pure native iron is very rare, and most of the specimens said to be such, have not been well attested. It has been found filling a vein in a mass of mica slate by Major Burrall on Canaan Mountain, Connecticut, in North America. (Edin. Philos. Journal for October 1827, p. 154.) The iron of meteoric origin is impure; for all the masses hitherto examined contain nickel and cobalt. (Stromeyer.) Metallic iron is easily procured by heating the native oxide with charcoal; but when thus obtained, it is never quite free from carbonaceous matter. The only method of preparing iron absolutely pure, is by passing dry hydrogen gas over the pure oxide, heated to redness in a tube of porcelain.

Iron has a strong affinity for oxygen. In a perfectly dry atmosphere, it undergoes hardly any change; but when moisture is likewise present, it oxidizes or *rusts* in the course of a few days. Heated to redness in the open air, it absorbs oxygen rapidly, and is converted into black scales, called the *black oxide* of iron; and in an atmosphere of oxygen gas, it burns with vivid scintillations. It decomposes the vapour of water, by uniting with its oxygen, at all temperatures, from a dull red to a white heat; a singular fact when it is considered, that at the very same temperature, the oxides of iron are reduced to the metallic state by hydrogen gas. (Gay-Lussac in An. de Ch. et de Physique, i. 36.)

## *Oxides of Iron.*

Iron combines with oxygen in two proportions only, forming the blue or protoxide, and the red or peroxide of iron. Both these compounds are capable of yielding regular crystallizable salts with acids.

*Protoxide.*—This oxide is the base of the native carbonate of iron, and of the green vitriol of commerce. Its existence was inferred some years ago by Gay-Lussac, (An. de Ch. Vol. lxxx;) but Stromeyer first obtained it in an insulated form by transmitting dry hydrogen gas over the peroxide of iron at a very low temperature. (Edinburgh Journal of Science, No. x.)

The protoxide of iron has a dark blue colour, and when melted with vitreous substances communicates to them a tint of blue. It is attracted by the magnet, though less powerfully than metallic iron. It is exceedingly combustible; for when fully exposed to air at common temperatures, it suddenly takes fire and burns vividly, being reconverted into the peroxide. Its salts, particularly when in solution, absorb oxygen from the atmosphere with such rapidity, that they may even be employed in eudiometry. This protoxide is always formed with evolution of hydrogen gas, when metallic iron is put into dilute sulphuric or muriatic acid; and its composition may be determined by collecting and measuring the gas which is disengaged. According to Gay-Lussac, it is composed of 8 parts of oxygen, and 28.3 parts of iron; but Dr Thomson infers from an analysis of the protosulphate of iron, that the quantity of iron united with 8 parts of oxygen is 28 precisely. The atomic weight of the protoxide is therefore 36.

The protoxide of iron is precipitated as a white hydrate by pure alkalies, as a white carbonate by alkaline carbonates, and as a white ferrocyanate by ferrocyanate of potassa. The two former precipitates become first green and then red, and the latter, green and blue by exposure to the air. The solution of gall-nuts produces no change of colour. Sulphuretted hydrogen does not act, if the protoxide is united with any of the stronger acids; but the alkaline hydrosulphurets cause a black precipitate, the protosulphuret of iron.

*Peroxide.*—The red or peroxide is a natural product, known to mineralogists under the name of *red hematite*. It sometimes occurs massive, at other times fibrous, and occasionally in the form of beautiful rhomboidal crystals. It may be made chemically by dissolving iron in nitro-muriatic acid, and adding an alkali. The hydrate of the red oxide of a brownish-red colour subsides, which is identical in composition with the mineral called *brown hematite*, and consists of 40 parts or one equivalent of the peroxide, and 9 parts or one equivalent of water.

The peroxide of iron is not attracted by the magnet. Fused with vitreous substances, it communicates to them a red or yellow colour. It combines with most of the acids, forming salts, the greater number of which are red. Its presence may be detected by very decisive tests. The pure alkalies, fixed or volatile, precipitate it as the hydrate. The alkaline carbonates have a similar effect, for the peroxide of iron does not form a permanent salt with carbonic acid. With ferrocyanate of potassa, it forms Prussian blue, the ferrocyanate of the peroxide of iron. The sulphocyanate of potassa causes a deep blood-red, and infusion of gall-nuts, a black colour. Sulphuretted hydrogen converts the peroxide into the protoxide of iron, and deposition of sulphur takes place at the same time. These reagents, and especially the ferrocyanate and sulphocyanate of potassa, afford an unerring test of the presence of minute quantities of the peroxide of iron. On this account it is customary, in testing for iron, to convert it into the peroxide, which is easily effected by boiling the solution with a small quantity of nitric acid.

The researches of several chemists, such as Gay-Lussac, Berzelius, Bucholz, and Thomson, leave no doubt that the oxygen contained in the blue and red oxides of iron is in the ratio of one to one and a half. Consequently, the peroxide consists of 28 parts or one equivalent of iron, and 12 parts or an equivalent and a half of oxygen.

*Black Oxide.*—This substance, long supposed to be the protoxide of iron, contains more oxygen than the blue, and less than the red oxide. It cannot be regarded as a definite compound of iron and oxygen; but is composed of the two real oxides, united in a proportion which is by no means constant. It occurs native, frequently crystallized in the form of a regular octahedron, which is not only attracted by the magnet, but is itself sometimes magnetic. It is always formed when iron is heated to redness in the open air; and is likewise generated by the contact of watery vapour with iron at elevated temperatures. The composition of the product, however, varies with the duration of the process and the temperature which is employed. Thus, according to Bucholz, Berzelius, and Thomson, 100 parts of iron, when oxidized by steam, unite with nearly 30 of oxygen; whereas in a similar experiment performed by Gay-Lussac, 37.8 parts of oxygen were absorbed. The oxide of Gay-Lussac may be regarded as a compound of one equivalent of the protoxide and two equivalents of the peroxide; and Berzelius is of opinion that the composition of magnetic iron ore is similar. M. Mosander states, that on heating a bar of iron in the open air, the outer layer of the scales contains a greater quantity of peroxide than the inner layer. The former consists of one equivalent of peroxide to two of the protoxide, an in the latter are contained one equivalent of peroxide to three equivalents of protoxide. The inner layer seems uniform in composition; but the outer is variable, its more exposed parts being richer in oxygen.

The nature of the black oxide is further elucidated by the action of acids. On digesting the black oxide in sulphuric acid, an olive-colour-

ed solution is formed, containing two salts, sulphate of the peroxide and protoxide, which may be separated from each other by means of alcohol (Proust and Gay-Lussac.) These mixed salts give green precipitates with alkalies, and a very deep blue ink with an infusion of gall-nuts. The black oxide of iron is the cause of the dull green colour of bottle glass.

*Chlorides of Iron.*—Chlorine unites in two proportions with iron, forming compounds which were described in 1812 by Dr John Davy. The protochloride is made by evaporating a solution of the proto-muriate to dryness, and heating it to redness in a glass tube from which the air is excluded. The resulting chloride has a gray colour, a lamellated texture, and metallic lustre. It is composed of one proportional of each element, and is converted by water into the proto-muriate of iron.

The perchloride is formed by burning iron wire in an atmosphere of chlorine. It is of a bright yellowish-brown colour, crystallizes in small iridescent plates, and is volatile at a temperature a little above 212° F. It consists of one equivalent of iron and an equivalent and a half of chlorine, and forms with water a red-coloured solution, which is the permuriate of iron.

An *iodide of iron* may be formed by heating iron in the vapour of iodine. It is converted by water into the hydriodate.

*Sulphurets of Iron.*—There are two compounds of iron and sulphur, both of which are natural products. The protosulphuret is the magnetic iron pyrites of mineralogists. It is a brittle yellow substance, of a metallic lustre, and is feebly attracted by the magnet. By exposure to air and moisture, it is gradually converted into the protosulphate of iron. It may be made artificially by igniting the protosulphate of iron with charcoal; or still more conveniently by heating a mixture of iron filings and sulphur. (Page 244.) It is dissolved completely and readily by dilute sulphuric or muriatic acid, with disengagement of sulphuretted hydrogen. It is composed of 28 parts or one equivalent of iron, and 16 parts or one equivalent of sulphur.

The bisulphuret, which contains two equivalents of sulphur, is the common iron pyrites. When heated to redness, it loses half its sulphur, and is converted into the protosulphuret. It is insoluble in sulphuric and muriatic acid.

*Phosphuret of Iron.*—This compound may be formed by heating the phosphate of iron with charcoal. It is sometimes contained in metallic iron, to the properties of which it is exceedingly injurious, by causing it to be brittle at common temperatures.

*Carburets of Iron.*—Carbon and iron unite in very various proportions; but there are four compounds which are distinct from one another, namely, cast or pig iron, steel, cast steel, and graphite or plumbago.

The native oxides of iron, which commonly contain argilaceous and siliceous substances, are reduced to the metallic state by the action of coke or charcoal and lime at a high temperature. The oxygen of the oxide of iron unites with one portion of carbon, and the metal with another, yielding carbonic acid and carburet of iron; while the earthy substances together with a little oxide of iron enter into combination, forming a vitreous substance called *slag*, which rises to the surface. The fused carburet is then drawn off by an aperture at the bottom of the furnace, and received in hollows or moulds made with sand. In this state, it is neither ductile nor malleable, but very brittle; and fuses with such facility at a red heat that it cannot be welded. It is highly crystalline, and its texture is granular. It contains about 1-43d of its weight of carbon, together with small quantities of manganese, cal-

cium, silicium, and probably aluminium; and besides these substances, which are chemically combined with the iron, particles of charcoal, earthy matters, and unreduced ore, are frequently inclosed within it.

Cast iron is converted into malleable iron by exposure, in a reverberatory furnace, to the combined action of air and intense heat. During this process all the undecomposed ore is reduced, earthy matters rise to the surface as slag, and the carbon is oxidized. As the purity of the iron increases, its fusibility diminishes, until at length, though the temperature remains the same, the iron becomes solid. It is then subjected, while still hot, to the operation of rolling or hammering, by which its particles are approximated. The metal, thus procured, is no longer a carburet, but is the purest iron of commerce. It is not, however, absolutely pure; for Berzelius has detected in it about one-half per cent of carbon, and it likewise appears to contain silicium.

Steel is made by exposing bars of the purest malleable iron, surrounded with charcoal in powder, to a long-continued red heat. During this process, the iron unites with about 1-150th of its weight of carbon, and acquires new properties. In ductility and malleability, it is far inferior to iron; but exceeds it greatly in hardness, sonorousness, and elasticity. Its texture is more compact than that of iron, and it is susceptible of a far higher polish. It bears a strong red heat without entering into fusion, and may be welded with iron. When combined with an additional quantity of carbon, it forms cast steel. In this state, it is harder and more elastic, has a closer texture, and receives a higher polish than common steel. It is so fusible, however, that it cannot be welded.

Steel differs chemically from cast iron in being composed of purer iron, and in containing a smaller proportion of carbon. It is readily distinguished from malleable iron by the action of an acid. When a drop of dilute muriatic acid is placed on steel, a black spot appears, in consequence of a portion of iron being dissolved, while the charcoal is left.

Graphite, more commonly known under the name of plumbago or black lead, is a native carburet of iron, which contains 95 per cent of carbon. It is unchangeable in the air, and like pure charcoal is attacked with difficulty by chemical substances. It has an iron-gray colour, metallic lustre, and granular texture. Its chief use is in making pencils and crucibles, and in burnishing iron to protect it from rust.

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# SECTION XIII.

## *ZINC.—CADMIUM.*

### *Zinc.*

The zinc of commerce, sometimes called *spelter*, is obtained either from *calamine* the native carbonate of zinc, or from the native sulphuret, the *zinc blende* of mineralogists. It is procured from the former by heat and carbonaceous matters; and from the latter by a similar process after the ore has been previously oxidized by *roasting*, that is, by exposure to the air at a low red heat. When first extracted

from its ores, it is never quite pure; but contains charcoal, sulphur, and several metals in small quantity. It may be freed from these impurities by distillation,—by exposing it to a white heat in an earthern retort, to which a receiver full of water is adapted.

Zinc has a strong metallic lustre, and a bluish-white colour. Its texture is lamellated, and its density about 7. It is a hard metal, being acted on by the file with difficulty. At low or high degrees of heat it is brittle; but at temperatures between 210° and 300° F, it is both malleable and ductile, a property which enables zinc to be rolled or hammered into sheets of considerable thinness. It fuses at 680° F, and when slowly cooled assumes regular forms. Exposed in close vessels to a white heat, it sublimes unchanged.

Zinc undergoes little change by the action of air and moisture. When fused in open vessels, it absorbs oxygen, and forms the white oxide, called flowers of zinc. Heated to full redness in a covered crucible, it bursts into flame as soon as the cover is removed, and burns with a brilliant white light. The combustion ensues with such violence, that the oxide as it is formed is mechanically carried up into the air. Zinc is readily oxidized by dilute sulphuric or muriatic acid, and the hydrogen which is evolved contains a small quantity of metallic zinc in combination.

*Oxide of Zinc.*—Chemists are acquainted with one compound only of zinc and oxygen, and this oxide is formed under all the circumstances just mentioned. At common temperatures it is white; but when heated to low redness, it assumes a yellow colour, which gradually disappears on cooling. It is quite fixed in the fire. It is insoluble in water, and therefore does not affect the blue colour of plants; but it is a strong salifiable base, forming regular salts with acids, most of which are colourless. It combines also with some of the alkalies. According to the analysis of Dr Thomson, it is composed of

| | | |
|---|---|---|
| Zinc . | 34 . . | one equivalent. |
| Oxygen . | 8 . . | one equivalent. |

And hence 42 is its combining proportion.

The presence of zinc is easily recognised by the following characters.—The oxide is precipitated from its solutions as a white hydrate by pure potassa or ammonia, and as carbonate by carbonate of ammonia, but is completely redissolved by an excess of the precipitant. The fixed alkaline carbonates precipitate it permanently as white carbonate of zinc. Hydrosulphuret of ammonia causes a white precipitate, which is either a hydrosulphuret of the oxide of zinc, or a hydrated sulphuret of the metal. Sulphuretted hydrogen acts in a similar manner, if the solution is quite neutral; but it has no effect if an excess of any strong acid is present.

The *Chloride or Butter of Zinc* was made by Dr J. Davy by evaporating the muriate to dryness, and then heating it to redness in a glass tube. It deliquesces on exposure to the air, being reconverted into a muriate. It is composed of one equivalent of chlorine and one equivalent of zinc.

The native sulphuret of zinc, or zinc blende, is frequently found in dodecahedral crystals, or in forms allied to the dodecahedron. Its structure is lamellated, its lustre adamantine, and its colour variable, being sometimes yellow, red, brown, or black. It may be made artificially by heating to redness a mixture of oxide of zinc and sulphur, by decomposing sulphate of zinc by charcoal, or by drying the white

precipitate obtained on adding hydrosulphuret of ammonia to a salt of zinc.

Sulphuret of zinc is composed of one proportional of each of its constituents, and is dissolved with disengagement of sulphuretted hydrogen gas by dilute muriatic or sulphuric acid.

## *Cadmium.*

Cadmium was discovered in the year 1817 by Stromeyer in an oxide of zinc which had been prepared for medical purposes*; and he has since found it in several of the ores of that metal, especially in a radiated blende from Bohemia which contains about five per cent of cadmium. The late Dr Clarke detected its existence in some of the zinc ores of Derbyshire, and in the common zinc of commerce. Mr Herapath has found it in considerable quantity in the zinc works near Bristol†. During the reduction of calamine by coal, the cadmium, which is very volatile, flies off in vapour, mixed with soot and some oxide of zinc, and collects in the roof of the vault, just above the tube leading from the crucible. Some portions of this substance yielded from twelve to twenty per cent of cadmium.

The process by which Stromeyer separates cadmium from zinc or other metals is the following. The ore of cadmium is dissolved in dilute sulphuric or muriatic acid, and after adding a portion of free acid, a current of sulphuretted hydrogen gas is transmitted through the liquid, by means of which the cadmium is precipitated as sulphuret, while the zinc continues in solution. The sulphuret of cadmium is then decomposed by nitric acid, and the solution evaporated to dryness. The dry nitrate of cadmium is dissolved in water, and an excess of carbonate of ammonia added. The white carbonate of cadmium subsides, which, when heated to redness, yields a pure oxide. By mixing this oxide with charcoal, and exposing the mixture to a red heat, metallic cadmium is sublimed.

A very elegant process for separating zinc from cadmium was proposed by Dr Wollaston. The solution of the mixed metals is put into a platinum capsule, and a piece of metallic zinc is placed in it. If cadmium is present, it is reduced, and adheres so tenaciously to the capsule, that it may be washed with water without danger of being lost. It may then be dissolved either by nitric or dilute muriatic acid.

Cadmium, in colour and lustre, has a strong resemblance to tin, but is somewhat harder and more tenacious. It is very ductile and malleable. Its specific gravity is 8.604 before being hammered, and 8.694 afterwards. It melts at about the same temperature as tin, and is nearly as volatile as mercury, condensing like it into globules which have a metallic lustre. Its vapour has no odour.

When heated in the open air, it absorbs oxygen, and is converted into an oxide. Cadmium is readily oxidized and dissolved by nitric acid, which is its proper solvent. Sulphuric and muriatic acids act upon it less easily, and the oxygen is then derived from water.

Cadmium combines with oxygen, so far as is yet known, in one proportion only; and this oxide is conveniently procured in a separate state by igniting the carbonate. It has an orange colour, and is fixed in the fire. It is insoluble in water, and does not change the colour of violets; but it is a powerful salifiable base, forming neutral salts with

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* Annals of Philosophy, vol. xiv. † Ibid. N.S. vol. iii.

acids. This oxide, according to the analysis of Stromeyer, is composed of 56 parts of cadmium and 8 parts of oxygen. It is of course regarded as a compound of one proportional of each element, and consequently 56 is the equivalent of cadmium.

The oxide of cadmium is precipitated as a white hydrate by pure ammonia, but is redissolved by excess of the alkali. It is precipitated permanently by pure potassa as a hydrate, and by all the alkaline carbonates as carbonate of cadmium.

The sulphuret of cadmium, which occurs native in some kinds of zinc blende, is easily procured by the action of sulphuretted hydrogen on a salt of cadmium. It has a yellowish-orange colour, and is distinguished from the sulphuret of arsenic by being insoluble in pure potassa, and by sustaining a white heat without subliming. It is composed of 56 parts or one equivalent of cadmium, and 16 parts or one equivalent of sulphur. (Stromeyer.)

The chloride of cadmium may be prepared by decomposing the muriate by heat.

## SECTION XIV.

### *TIN.*

The tin of commerce, known by the names of block and grain tin, is procured from the native oxide by means of heat and charcoal. The best grain tin is almost chemically pure, containing, according to Dr Thomson, very minute quantities of copper and iron, and occasionally of arsenic.

Tin has a white colour, and a lustre resembling that of silver. The brilliancy of its surface is soon impaired by exposure to the atmosphere, though it is not oxidized even by the combined agency of air and moisture. Its malleability is very considerable; for the thickness of common tin-foil does not exceed 1-1000th of an inch. In ductility and tenacity it is inferior to several metals. It is soft and inelastic, and when bent backwards and forwards, emits a peculiar crackling noise. Its specific gravity is about 7.9. At 442° F. it fuses, and if exposed at the same time to the air, its surface tarnishes, and a gray powder is formed. When heated to whiteness, it takes fire and burns with a white flame, being converted into the peroxide of tin.

*Oxides of Tin.*—Tin is susceptible of two degrees of oxidation. Both the oxides of tin form salts by uniting with acids; but they are likewise capable of combining with alkalies. From data furnished by the experiments of Berzelius, Gay-Lussac, and Thomson, these oxides are inferred to be thus constituted :—

| | *Tin.* | *Oxygen.* |
|---|---|---|
| Protoxide | 58 or one equivalent. | 8 or one equivalent. |
| Peroxide | 58 . . . . | 16 or two equivalents. |

The protoxide is of a gray colour, and is formed when tin is kept for some time in a state of fusion in an open vessel. It may also be procured by precipitation from the protomuriate of tin. This salt is made by boiling tin in strong muriatic acid, when the metal is oxidized by the decomposition of water; and if atmospheric air be carefully excluded, a pure protomuriate results. From this solution the hydrate of the protoxide may be precipitated, either by pure po-

tassa or the carbonate of that alkali; but an excess of the former must be carefully avoided, as otherwise the precipitate would be redissolved. It is essential likewise to the success of the process, that the protoxide should be both washed and dried without being exposed to the air.

The protoxide of tin is remarkable for its powerful affinity for oxygen. When heated in open vessels, it is converted into the peroxide with evolution of heat and light. Its salts not only attract oxygen from the air, but act as powerful deoxidizing agents. Thus the protomuriate of tin converts the peroxide of copper or iron into protoxides, and precipitates silver, mercury, and platinum from their solutions in the metallic state. Added to a solution of gold, it occasions a purple-coloured precipitate, the *purple of Cassius*, which is a compound of the peroxide of tin and protoxide of gold. By this character the protoxide of tin is recognised with certainty. It is thrown down by sulphuretted hydrogen as the black protosulphuret of tin.

The peroxide of tin is most conveniently prepared by the action of nitric acid on metallic tin. Nitric acid, in its most concentrated state, does not act easily upon tin; but when a small quantity of water is added, violent effervescence takes place, owing to the evolution of nitrous acid and the deutoxide of nitrogen, and a white powder, the hydrated peroxide is produced. On edulcorating this substance, and heating it to redness, watery vapour is expelled, and the pure peroxide, of a straw yellow colour, remains. In this process ammonia is generated, a circumstance which proves water as well as nitric acid to have been decomposed.

The peroxide of tin has a very feeble affinity for acids. With nitric acid it does not unite at all; and as prepared by the preceding method, it is dissolved by muriatic acid, even before being ignited, with great difficulty. The permuriate of tin may, however, be formed by the action of nitro-muriatic acid on metallic tin, aided by a gentle heat. In this manner is obtained the solution of tin employed as a mordant in dyeing.

The peroxide of tin is separated from its solution in muriatic acid as a bulky hydrate by potassa, ammonia, or the alkaline carbonates, and the precipitate is easily and completely redissolved by the pure fixed alkali in excess. Sulphuretted hydrogen occasions a yellow precipitate, which is either the hydrosulphuret of the peroxide of tin, or the bisulphuret of the metal.

The peroxide of tin, when melted with glass, forms white enamel.

*Chlorides of Tin.*—Tin unites in two proportions with chlorine, and the researches of Dr Davy leave no doubt of these compounds being analogous in composition to the oxides of tin.

The protochloride, which consists of one equivalent of tin and one equivalent of chlorine, may be made either by evaporating the muriate of the protoxide to dryness and fusing the residue in a close vessel, or by heating an amalgam of tin with calomel. (Dr Davy.) It is a gray solid substance, of a resinous lustre, which fuses at a heat below redness, and when heated in chlorine gas is converted into the bichloride.

The bichloride, composed of one equivalent of tin and two equivalents of chlorine, may be prepared either by heating metallic tin or the protochloride in an atmosphere of chlorine, or by distilling a mixture of eight parts of tin in powder with twenty-four of corrosive sublimate. It is a colourless volatile liquid, which emits copious white fumes when exposed to the atmosphere. It has a very strong attrac-

tion for water, and is converted by that fluid into the permuriate. It was formerly called the *fuming liquor of Libavius*.

*Sulphurets of Tin.*—The protosulphuret is best formed by heating sulphur with metallic tin. A brittle compound of a bluish-gray colour and metallic lustre results, which is fusible at a red heat, and assumes a lamellated structure in cooling. It is dissolved by muriatic acid, with disengagement of sulphuretted hydrogen. According to the analysis of Dr Davy and Berzelius, it is composed of one equivalent of tin and one equivalent of sulphur.

The bisulphuret, formerly called *aurum musivum*, has a golden yellow colour, and is made by heating a mixture of sulphur and peroxide of tin in close vessels. The elements of the latter unite with separate portions of sulphur, forming sulphurous acid and bisulphuret of tin. This compound was supposed by Proust to be the hydrosulphuret of the peroxide of tin, and its real nature was first made known by Dr Davy. (Philos. Trans. for 1812, page 198.) It consists of one equivalent of tin and two equivalents of sulphur.

By exposing a mixture of sulphur and protosulphuret of tin to a low red heat, Berzelius obtained a compound consisting of 58 parts or one equivalent of tin, and 24 parts or one equivalent and a half of sulphur. If it is really a definite compound, it should be termed a *sesquisulphuret*.

# CLASS II.

## ORDER II.

### *METALS WHICH DO NOT DECOMPOSE WATER AT ANY TEMPERATURE, AND THE OXIDES OF WHICH ARE NOT REDUCED TO THE METALLIC STATE BY THE SOLE ACTION OF HEAT.*

## SECTION XV.

### *ARSENIC.*

Metallic arsenic sometimes occurs native, but more frequently it is found in combination with other metals, and especially with cobalt and iron. On roasting these arsenical ores in a reverberatory furnace, the arsenic, from its volatility, is expelled, combines with oxygen as it rises, and condenses into thick cakes on the roof of the chimney. The sublimed mass, after being purified by a second sublimation, is the virulent poison known by the name of *arsenic*, or *white oxide of arsenic*. From this substance the metal itself is procured by heating it with charcoal. The most convenient process is to mix the white oxide with about twice its weight of black flux, and expose the mixture to a red heat in a Hessian crucible, over which is luted an empty crucible for receiving the metal. The reduction is easily effected,

and metallic arsenic collects in the upper crucible, which should be kept cool for the purpose of condensing the vapour.

Arsenic is an exceedingly brittle metal, of a strong metallic lustre, and white colour, running into steel-gray. Its structure is crystalline, and its density 8.3*. When heated to 356° F., it sublimes without previously liquefying; for its point of fusion is far above that of its sublimation, and has not hitherto been determined. Its vapour has a strong odour of garlic, a property which affords a distinguishing character for metallic arsenic, as it is not possessed by any other metal, with the exception perhaps of zinc, which is said to emit a similar odour when thrown in powder on burning charcoal. In close vessels, it may be sublimed without change, but if atmospheric air be admitted, it is rapidly converted into the white oxide. It soon tarnishes by exposure to the atmosphere at common temperatures, acquiring a dark film upon its surface. This crust, which is exceedingly superficial, was supposed by Berzelius to be a distinct oxide; but it is more generally regarded as a mixture of white oxide and metallic arsenic.

## *Compounds of Arsenic and Oxygen.*

Chemists are acquainted with two compounds of arsenic and oxygen, and as they both possess the properties of an acid, the terms *arsenious* and *arsenic* acid have been properly applied to them. Considerable difference of opinion exists as to their composition. Dr Thomson believes 38 to be the combining proportion of metallic arsenic, and that arsenious acid consists of one atom of metal to two atoms of oxygen, and arsenic acid, of one atom of metal to three atoms of oxygen. According to Berzelius, 37.627 is the equivalent of the metal, and the oxygen in the two acids is in the ratio of 3 to 5. Arsenious acid is stated by the former to contain 29.63, and by the latter 24.18 per cent of oxygen, a difference which is very considerable. The results of Dr Thomson are commonly adopted in this country; but as several circumstances induce me to suspect their accuracy, I shall employ those of Berzelius by preference. As the atomic weight of metallic arsenic was found nearly the same by both chemists, 38 may be adopted as the most convenient. The composition of the two acids of arsenic may accordingly be thus stated:—

| | *Arsenic.* | *Oxygen.* |
|---|---|---|
| Arsenious acid | 38 or one equiv. | 12 or one and a half equiv. |
| Arsenic acid | 38 or one equiv. | 20 or two and a half equiv. |

*Arsenious Acid.*—This compound, frequently called *white oxide of arsenic*, is always generated when arsenic is heated in open vessels, and may be prepared by digesting the metal in dilute nitric acid. At 380° it is volatilized, yielding vapours which do not possess the odour of garlic, and which condense unchanged on cold surfaces. If the sublimation is conducted slowly, the vapour is deposited in the form of distinct octahedral crystals of adamantine lustre, and perfectly transparent. If the arsenious acid is suddenly heated beyond its subliming point, it fuses into a transparent brittle glass, which gradually becomes opake by keeping. The specific gravity of this glass is about 3.7.

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* According to Guibourt, the density of arsenic is 5.9. This number is adopted by Thenard, who considers it as more accurate than 8.3, the number obtained by Bergmann. B.

The taste of arsenious acid is stated differently by different persons. It is prevalently thought to be acrid; but I am satisfied from personal observation that it may be deliberately tasted, without exciting more than a very faint impression of sweetness, and perhaps of acidity. The acrid taste ascribed to it has probably been confounded with the local inflammation, by which its application, if of some continuance, is followed. (Dr Christison on the Taste of Arsenic in the Edinburgh Medical and Surgical Journal for July 1827.) It reddens vegetable blue colours feebly, an effect which is best shown by placing the acid in powder on moistened litmus paper. It combines with salifiable bases, forming salts which are termed *arsenites.*

According to the experiments of Klaproth and Bucholz, 1000 parts of boiling water dissolve 77.75 of arsenious acid; and the solution, after having cooled to 60° F. contains only 30 parts. The same quantity of water at 60, when mixed with the acid in powder, dissolves only two parts and a half.

The tests which are commonly recommended for detecting the presence of arsenious acid are four in number; namely, lime-water, the ammoniacal nitrate of silver, the ammoniacal sulphate of copper, and sulphuretted hydrogen.

1. When lime-water is added in excess to a solution of arsenious acid, a white precipitate subsides, which is the arsenite of lime. On drying this salt, mixing it with powdered charcoal or black flux, and heating the mixture contained in a glass tube to redness by means of a spirit lamp, the arsenic is reduced, sublimes, and condenses in a cool part of the tube. The process of reduction is absolutely necessary, since several other acids as well as the arsenious, such as the carbonic, phosphoric, oxalic, and tartaric acids, yield white precipitates with lime-water. The arsenite of lime is soluble in all acids which are capable of dissolving lime itself. Indeed all the arsenites are dissolved by those acids, with which their bases do not form insoluble compounds.

Lime-water is of little service for discovering arsenious acid in mixed fluids. For the arsenite of lime is so light a powder, that when formed in gelatinous or oleaginous solutions, such as in broth, or tea made with milk, it remains suspended in the liquid, and cannot be separated from it.

2. Arsenious acid is not precipitated by nitrate of silver unless an alkali be present, which may unite with the nitric acid. Ammonia is commonly employed for the purpose; but as the arsenite of silver is very soluble in ammonia, an excess of the alkali might retain the arsenite of silver in solution. To remedy this inconvenience, Mr Hume proposes to employ the ammoniacal nitrate of silver, which is made by dropping ammonia into a solution of lunar caustic, till the oxide of silver at first thrown down is nearly all dissolved. The liquid thus prepared contains the precise quantity of ammonia which is required; and when mixed with arsenious acid, two neutral salts result, the soluble nitrate of ammonia, and the insoluble yellow arsenite of silver. The ammoniacal nitrate of silver likewise diminishes the risk of fallacy that might arise from the presence of phosphoric acid. The phosphate of silver is so very soluble in ammonia, that when a neutral phosphate is mixed with the ammoniacal nitrate of silver, the resulting phosphate of silver is held almost entirely in solution by the free ammonia.

The test of nitrate of silver, however, even in its improved state, is still liable to objection. For when arsenious acid in small proportion is mixed with salts of muriatic acid, or animal and vegetable infusions,

the arsenite of silver either does not subside at all, or is precipitated in so impure a state that its characteristic colour cannot be distinguished. Several methods have been proposed for obviating this source of fallacy; but Dr Christison has shown, as I conceive quite satisfactorily, that this test cannot be relied on in practice.

3. The ammoniacal sulphate of copper, which is made by adding ammonia to a solution of sulphate of copper, until the precipitate, at first thrown down, is nearly all redissolved, occasions with arsenious acid a green precipitate, which has been long used as a pigment under the name of *Scheele's green.* This test, though well adapted for detecting arsenious acid dissolved in pure water, is very fallacious when applied to mixed fluids. Dr Christison has proved that the ammoniacal sulphate of copper produces in some animal and vegetable infusions, containing no arsenic, a greenish precipitate, which may be mistaken for Scheele's green; whereas in other mixed fluids, such as tea and porter, to which arsenic has been previously added, it occasions none at all, if the arsenious acid is in small quantity. In some of these liquids, a free vegetable acid is doubtless the solvent; but the arsenite of copper is also dissolved by tannin, and perhaps by other vegetable as well as some animal principles.

4. When a current of sulphuretted hydrogen gas is conducted through a solution of arsenious acid, the fluid immediately acquires a yellow colour, and in a short time becomes turbid, owing to the formation of orpiment, or the yellow sulphuret of arsenic. The precipitate is at first partially suspended in the liquid; but as soon as the free sulphuretted hydrogen is expelled by boiling, it subsides perfectly, and may easily be collected on a filter. One condition, however, must be observed in order to insure success, namely, that the liquid does not contain a free alkali; for the sulphuret of arsenic is dissolved with remarkable facility by pure potassa or ammonia. To avoid this source of fallacy, it is necessary to acidulate the solution with a little acetic or muriatic acid. Sulphuretted hydrogen likewise acts on arsenic in all vegetable and animal fluids, if previously boiled, filtered, and acidulated.

But it does not necessarily follow, because sulphuretted hydrogen causes a yellow precipitate, that arsenic is present; for there are not less than four other substances, namely, selenium, cadmium, tin, and antimony, the sulphurets of which, judging from their colour alone, might be mistaken for orpiment. From these and all other substances whatever, the sulphuret of arsenic may be thus distinguished.—When heated with black flux in the manner described for reducing the arsenite of lime, a metallic crust of an iron-gray colour externally, and crystalline on its inner surface, is deposited on the cool part of the tube; and by converting a portion of this crust into vapour, its alliaceous odour will instantly be perceived. Besides these circumstances, which alone are quite satisfactory, it is easy to procure additional evidence by reconverting the metal into arsenious acid, so as to obtain it in the form of resplendent octahedral crystals. This is done by holding that part of the tube to which the arsenic adheres, about three-fourths of an inch above a very small spirit lamp flame, so that the metal may be slowly sublimed. As it rises in vapour, it combines with oxygen, and is deposited in crystals within the tube. The character of these crystals with respect to volatility, lustre, transparency, and form, is so exceedingly well marked, that a practised eye may safely identify them, though their weight should not exceed the 100th part of a grain. This experiment does not succeed, unless the tube be quite clean and dry.

It hence appears, that of the various tests for arsenic, the only one

which gives uniform results, and is applicable to every case, is sulphuretted hydrogen:—all the rest may be dispensed with. For this great improvement in the mode of testing for arsenious acid, we are indebted to Dr Christison. By this process, he discovered the presence of arsenious acid when mixed with complex fluids, such as tea, porter, and the like, in the proportion of one-fourth of a grain to an ounce; and more recently he has twice obtained so small a quantity as the 20th of a grain from the stomachs of people who had been poisoned with arsenic. (Edinburgh Medical and Surgical Journal for October 1824; and second volume of the Transactions of the Medico-Chirurgical Society of Edinburgh.)

The black flux employed in the processes for reducing arsenic, is prepared by deflagrating a mixture of the bitartrate of potassa with half its weight of nitre. The nitric and tartaric acids undergo decomposition, and the solid product is charcoal derived from tartaric acid, and pure carbonate of potassa. When this substance is employed in the reduction of arsenious acid or its salts, the charcoal is of course the chief ingredient; but the alkali is of use in retaining the arsenious acid, until the temperature is sufficiently high for its decomposition. With sulphuret of arsenic, on the contrary, the alkali is the active principle, the potassium of which unites with sulphur and liberates the arsenic; but the charcoal operates usefully by facilitating the decomposition of the alkaline carbonate.

*Arsenic Acid.*—This compound is made by dissolving arsenious acid in concentrated nitric, mixed with a little muriatic acid, and distilling the solution to perfect dryness. The acid thus prepared, has a sour metallic taste, reddens vegetable blue colours, and with alkalies forms neutral salts, which are termed *arseniates*. It is much more soluble in water than arsenious acid, dissolving in five or six times its weight of cold, and in a still smaller quantity of hot water. It forms irregular grains when its solution is evaporated, but does not crystallize. If strongly heated, it fuses into a glass which is deliquescent. When urged by a very strong red heat, it is resolved into oxygen and arsenious acid. It is an active poison.

Arsenic acid is decomposed by sulphuretted hydrogen gas, and yields a sulphuret of arsenic very like orpiment in colour, but containing a greater proportional quantity of sulphur. The soluble arseniates, when mixed with the nitrate of lead or silver, form insoluble arseniates, the former of which has a white, and the latter, a brick-red colour. They dissolve readily in dilute nitric acid, and when heated with charcoal yield metallic arsenic.

*Chloride of Arsenic.*—When arsenic in powder is thrown into a jar full of dry chlorine gas, it takes fire, and a chloride of arsenic is generated; and the same compound may be formed by distilling a mixture of six parts of corrosive sublimate with one of arsenic. It is a colourless volatile liquid, which fumes strongly on exposure to the air, hence called *fuming liquor of arsenic*, and is resolved by water into muriatic and arsenious acids. According to Dr J. Davy, it is composed of 60.48 parts of chlorine and 39.52 of arsenic, a proportion which does not correspond with the laws of combination, and therefore is doubtless inexact.

The following process has been lately proposed by M. Dumas. Into a tubulated retort is introduced a mixture of arsenious acid with ten times its weight of concentrated sulphuric acid; and after raising its temperature to near 212°, fragments of sea-salt are thrown in by the tubular. If the salt is added in successive small portions, scarcely any muriatic acid gas is evolved, and the pure chloride may be collected

in cooled vessels. Towards the end of the process, a little water frequently passes over with the chloride, but this hydrated portion does not mix with the anhydrous chloride, but swims on its surface. The hydrate may be decomposed, and a pure chloride obtained, by distilling the mixture from a sufficient quantity of concentrated sulphuric acid. M. Dumas considers this compound a protochloride of arsenic, so that it is probably different from that obtained by means of corrosive sublimate. (Quarterly Journal of Science, N. S. i. 235.)

*Arseniuretted Hydrogen.*—This gas, which was discovered by Scheele, is most conveniently prepared by digesting an alloy of tin and arsenic in muriatic acid. It is a colourless elastic fluid, of a fetid odour, resembling that of garlic. Its specific gravity is about 0.5. It extinguishes bodies in combustion, but it is itself kindled by them, and burns with a blue flame. It instantly destroys small animals that are immersed in it, and is poisonous in a high degree, having proved fatal to a German philosopher, the late M. Gehlen. With oxygen gas, it forms an explosive mixture, and is decomposed by chlorine with deposition of arsenic. It is not absorbed by water, nor does it possess acid properties. It has not hitherto been obtained in a pure state, being always mixed with hydrogen, and consequently its composition has not been exactly determined.

A solid compound of arsenic and hydrogen of a brownish colour was discovered by Sir H. Davy, and Gay-Lussac and Thenard. It is formed by the action of water on an alloy of potassium and arsenic; and it is also generated by attaching a piece of arsenic to the negative wire during the decomposition of water by a galvanic battery. Its composition is unknown.

*Sulphurets of Arsenic.*—Sulphur unites with arsenic in at least three proportions, forming compounds, two of which occur in the mineral kingdom, and are well known by the names of *realgar* and *orpiment*. Realgar or the protosulphuret may be formed artificially by heating arsenious acid with about half its weight of sulphur, until the mixture is brought into a state of perfect fusion. The cooled mass is crystalline, transparent, and of a ruby-red colour; and may be sublimed in close vessels without change. It is composed of 38 parts or one equivalent of arsenic, and 16 parts or one equivalent of sulphur.

Orpiment, or the *sesquisulphuret* of arsenic, may be prepared by fusing together equal parts of arsenious acid and sulphur; but the best mode of obtaining it quite pure is by transmitting a current of sulphuretted hydrogen gas through a solution of arsenious acid. Orpiment has a rich yellow colour, fuses readily when heated, and becomes crystalline on cooling, and in close vessels may be sublimed without change. It is dissolved with great facility by the pure alkalies, and yields colourless solutions. In composition it is proportional to arsenious acid; that is, it consists of 38 parts or one equivalent of arsenic, and 24 parts or one equivalent and a half of sulphur.

Orpiment is employed as a pigment, and is the colouring principle of the paint called *King's yellow*. M. Braconnot has proposed it likewise for dyeing silk, woollen, or cotton stuffs of a yellow colour. For this purpose the cloth is soaked in a solution of orpiment in ammonia, and then suspended in a warm apartment. The alkali evaporates, and leaves the orpiment permanently attached to the fibres of the cloth. (An. de Ch. et de Ph. vol. xii.)

The persulphuret of arsenic is prepared by transmitting sulphuretted hydrogen gas through a moderately strong solution of arsenic acid; or by saturating a solution of arseniate of potassa or soda with the same gas, and acidulating with muriatic or acetic acid. The oxygen of the

acid unites with the hydrogen of the gas, and persulphuret of arsenic subsides. In colour it is very similar to orpiment, is dissolved by pure alkalies, fuses by heat, and may be sublimed in close vessels without decomposition. It is proportional, in composition, to arsenic acid; that is, it consists of one equivalent of arsenic and two equivalents and a half of sulphur.

The experiments of Orfila have proved that the sulphurets of arsenic are poisonous, though in a much less degree than arsenious acid. The precipitated sulphuret is more injurious than native orpiment.

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# SECTION XVI.

## *CHROMIUM. MOLYBDENUM. TUNGSTEN. COLUMBIUM.*

### *Chromium.*

Chromium* was discovered in the year 1797 by Vauquelin† in a beautiful red mineral, the native chromate of lead. It has since been detected in the mineral called *chromate of iron*, a compound of the oxides of chromium and iron, which occurs abundantly in several parts of the continent, in America, and at Unst in Shetland. (Hibbert.)

Chromium, which has hitherto been procured in very small quantity, owing to its powerful attraction for oxygen, may be obtained by exposing the oxide of chromium mixed with charcoal to the most intense heat of a smith's forge. Its colour is white with a shade of yellow and distinct metallic lustre. It is a brittle metal, very infusible, and with difficulty attacked by acids, even by the nitro-muriatic. Its specific gravity has been stated at 5.9; but Dr Thomson found it a little above 5. When fused with nitre, it is oxidized, and converted into chromic acid.

Chromium unites with oxygen in two proportions, forming the green oxide, and chromic acid. Dr Thomson some years ago ascertained that the combining proportion of chromic acid is 52; and according to the results of an elaborate investigation, published in the Philosophical Transactions for 1827, the oxide and acid are thus constituted:—

| | *Chromium.* | *Oxygen.* |
|---|---|---|
| Green oxide | 32 or one equiv. | 8 or one equivalent. |
| Chromic acid | 32 . . | 20 or two and a half equiv. |

*Protoxide.*—This oxide is easily prepared by dissolving chromate of potassa in water, and mixing it with a solution of protonitrate of mercury, when an orange-coloured precipitate, the chromate of the protoxide of mercury, subsides. On heating this salt to redness in an earthen crucible, the mercury is dissipated in vapour, and the chromic acid is resolved into oxygen and protoxide of chromium.

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* From Χρωμα, *colour*, indicative of its remarkable tendency to form coloured compounds.

† Annales de Chimie, vol. xxv. and lxx.

Protoxide of chromium is of a green colour, exceedingly infusible, and suffers no change by heat. It is insoluble in water, and after being strongly heated, resists the action of the most powerful acids. Deflagrated with nitre, it is oxidized to its maximum, and is thus reconverted into chromic acid. Fused with borax or vitreous substances, it communicates to them a beautiful green colour, a property which affords an excellent test of its presence, and renders it exceedingly useful in the arts. The emerald owes its colour to the presence of this oxide.

Protoxide of chromium is a salifiable base, and its salts, which have a green colour, may be easily prepared in the following manner. To a boiling solution of chromate of potassa in water, equal measures of strong muriatic acid and alcohol are added in successive small portions, until the red tint of the chromic acid disappears entirely, and the liquid acquires a pure green colour. On pouring an excess of pure ammonia into this solution, a pale green bulky precipitate is formed, which consists of one equivalent of the protoxide and twenty-six equivalents of water. (Thomson.) The hydrate is readily dissolved by acids.

*Chromic Acid.*—This acid is prepared by digesting chromate of baryta in a quantity of dilute sulphuric acid exactly sufficient for combining with the baryta. The sulphate of baryta subsides, and a solution of chromic acid is obtained. Another method has been lately proposed by M. Arnold Maus, which consists in decomposing a hot concentrated solution of bichromate of potassa by silicated hydrofluoric acid. The chromic acid, after being separated from the sparingly soluble hydrofluate of silica and potassa, is evaporated to dryness in a platinum capsule, and then redissolved in the smallest possible quantity of water. By this means the last portions of the double salt are rendered insoluble, and the pure chromic acid is then separated by decantation. The acid must not be filtered in this concentrated state, as it then corrodes paper like sulphuric acid, and is converted into chromate of the green oxide of chromium. When it is wished to prepare a large quantity of chromic acid by this process, porcelain vessels may be safely employed in the first part of the operation; provided care is taken to add a quantity of silicated hydrofluoric acid not quite sufficient for precipitating the whole of the potassa. (Edinburgh Journal of Science, No. xvi. 175.)

Chromic acid has a dark ruby-red colour, and forms irregular crystals when its solution is concentrated. It is very soluble in water, has a sour taste, and possesses all the properties of an acid. It is converted into the green oxide, with evolution of oxygen, by exposure to a strong heat. It yields a muriate of the protoxide, when boiled with muriatic acid and alcohol, and the direct solar rays have a similar effect when muriatic acid is present. With sulphurous acid, it forms a sulphate of the protoxide.

Chromic acid is characterized by its colour, and by forming coloured salts with alkaline bases. The most important of these salts is the chromate of lead, which is found native in small quantity, and is easily prepared by mixing chromate of potassa with a soluble salt of lead. It is of a rich yellow colour, and is employed in the arts of painting and dyeing to great extent.

When sulphurous acid gas is transmitted into a solution of chromate or bichromate of potassa, a brown precipitate subsides, which was long regarded as a distinct oxide of chromium; but Dr Thomson, in the essay above cited, has proved that it is the green oxide combined with a little chromic acid. The acid may in a great measure be

washed away by means of water, and by ammonia it is entirely removed. The best mode of separating it, is to dissolve the brown matter with muriatic acid, and then precipitate the green oxide by ammonia.

*Fluochromic Acid Gas.*—When a mixture of fluor spar and chromate of lead is distilled with fuming or even common sulphuric acid in a leaden retort, a red coloured gas is disengaged. This gas acts rapidly upon glass, with deposition of chromic acid and formation of fluosilicic acid gas. It is absorbed by water, and the solution is found to contain a mixture of hydrofluoric and chromic acids. The watery vapour of the atmosphere effects its decomposition, so that when mixed with air, red fumes appear, owing to the separation of minute crystals of chromic acid. This gas may be regarded as a compound either of fluorine and chromium, or of hydrofluoric and chromic acids; but from the circumstance of its being decomposed so readily by moisture, the first view is the more probable.

*Chlorochromic Acid Gas.*—This compound is formed by the action of fuming sulphuric acid on a mixture of chromate of lead and chloride of sodium. It is a red coloured gas which may be collected in glass vessels over mercury. It is decomposed instantly by water, and yields a solution of muriatic and chromic acids. It may be regarded either as a compound of muriatic and chromic acids, or of chlorine and chromium.

These gases were discovered in the year 1825 by M. Unverdorben. (Edinburgh Journal of Science, No. vii. 129.)

Dr Thomson, in the essay already referred to, has described a red coloured liquid under the name of chlorochromic acid, which he obtained by the action of concentrated sulphuric acid on a mixture of dry bichromate of potassa and sea-salt. It obviously contains chromic acid and chlorine; but its exact nature has not been satisfactorily established, and I apprehend, from Dr Thomson's description, that it is not a definite compound.

## Molybdenum.

When the native sulphuret of molybdenum, in fine powder, is digested in nitro-muriatic acid until the ore is completely decomposed, and the residue is briskly heated in order to expel sulphuric acid, molybdic acid remains in the form of a white heavy powder. From this acid metallic molybdenum may be obtained by exposing it with charcoal to the strongest heat of a smith's forge; or by conducting over it a current of hydrogen gas, while strongly heated in a tube of porcelain. (Berzelius.)

Molybdenum is a brittle metal, very infusible, and of a white colour. It has hitherto been procured in small quantities only, and its properties are known imperfectly. When heated in open vessels, it absorbs oxygen, and is converted into *molybdic acid;* and the same compound is generated by the action of chlorine or nitro-muriatic acid. It has three degrees of oxidation, forming two oxides and one acid. The molybdic acid, according to Bucholz, is composed of 48 parts of molybdenum and 24 parts of oxygen; and, consequently, on the supposition that this acid contains three atoms of oxygen, 48 is the atomic weight of the metal itself.

Molybdic acid is a white powder, of specific gravity 3.4. It has a sharp metallic taste, reddens litmus paper, and forms salts with alkaline bases. It is very sparingly soluble in water; but the molybdates

of potassa, soda, and ammonia, dissolve in that fluid, and the molybdic acid is precipitated from the solutions by any of the strong acids.

Berzelius has lately described the two oxides of molybdenum. (Edinburgh Journal of Science, No. vii. 133.) The *protoxide* is black, and consists of one equivalent of oxygen and one equivalent of molybdenum. The *deutoxide* is brown, and contains twice as much oxygen as the protoxide. They both form salts with acids. Berzelius states that the blue *molybdous acid* of Bucholz, is a bimolybdate of the deutoxide of molybdenum.

Berzelius has likewise succeeded in forming three *chlorides* of molybdenum, the composition of which is analogous to the compounds of this metal with oxygen.

The native *sulphuret* of molybdenum, according to the analysis of Bucholz, is composed of 48 parts or one equivalent of molybdenum, and 32 parts or two equivalents of sulphur. Berzelius has lately discovered another sulphuret, of a ruby-red colour, transparent, and crystallized. It is proportional to the molybdic acid; that is, contains three equivalents of sulphur to one equivalent of the metal.

## *Tungsten.*

Tungsten may be procured in the metallic state by exposing tungstic acid to the action of charcoal or dry hydrogen gas at a red heat; but though the reduction is easily effected, an exceedingly intense temperature is required for fusing the metal. Tungsten has a grayish-white colour, and considerable lustre. It is brittle, nearly as hard as steel, and less fusible than manganese. Its specific gravity is near 17.4. When heated to redness in the open air, it takes fire, and is converted into tungstic acid; and it undergoes the same change by the action of nitric acid. Digested with a concentrated solution of pure potassa, it is dissolved with disengagement of hydrogen gas, and tungstate of potassa is generated.

Chemists are acquainted with two compounds of this metal and oxygen, namely, the *dark brown oxide*, and the *yellow acid of tungsten;* and according to the analyses of Berzelius, (An. de Ch. et de Ph. vol. xvii.) the oxygen of the former is to that of the latter in the ratio of two to three. It is hence inferred, that the real protoxide of tungsten is yet unknown, and that tungstic acid contains three atoms of oxygen to one atom of the metal. Now, Bucholz ascertained that this acid consists of 96 parts of tungsten and 24 parts of oxygen, and consequently 96 is the atomic weight of tungsten, and 120 the equivalent of its acid. The brown oxide is composed of 96 parts or one equivalent of metal, and 16 parts or two equivalents of oxygen.

A convenient method of preparing tungstic acid is by digesting the native tungstate of lime, very finely levigated, in nitric acid; by which means the nitrate of lime is formed, and the tungstic acid separated in the form of a yellow powder. Long digestion is required before all the lime is removed; but the process is facilitated by acting upon the mineral alternately by nitric acid and ammonia. The tungstic acid is dissolved readily by that alkali, and may be obtained in a separate state by heating the tungstate of ammonia to redness. Tungstic acid may also be prepared by the action of muriatic acid on *wolfram*, the native tungstate of iron and manganese. It is also obtained by heating the brown oxide to redness in open vessels.

Tungstic acid is of a yellow colour, is insoluble in water, and has no action on litmus paper. With alkaline bases, it forms salts called

*tungstates*, which are decomposed by the stronger acids, the tungstic acid in general falling combined with the acid by which it is precipitated. When strongly heated in open vessels, it acquires a green colour, and becomes blue when exposed to the action of hydrogen gas at a temperature of 500° or 600° F. The blue compound, according to Berzelius, is a tungstate of the oxide of tungsten; and the green colour is probably produced by an admixture of this compound with the yellow acid.

The oxide of tungsten is formed by the action of hydrogen gas on tungstic acid at a low red heat; but the best mode of procuring it both pure and in quantity, is that recommended by Wöhler. (Quarterly Journal of Science, xx. 177.) This process consists in mixing wolfram in fine powder with twice its weight of carbonate of potassa, and fusing the mixture in a platinum crucible. The resulting tungstate of potassa is dissolved in hot water, mixed with about half its weight of muriate of ammonia in solution, evaporated to dryness, and exposed in a Hessian crucible to a red heat. The mass is well washed with boiling water, and the insoluble matter digested in dilute potassa to remove any tungstic acid. The residue is oxide of tungsten. It appears that in this process the tungstate of potassa and muriate of ammonia mutually decompose each other, so that the dry mass consists of chloride of potassium and tungstate of ammonia. The elements of the latter react on each other at a red heat, giving rise to water, nitrogen gas, and oxide of tungsten; and this compound is protected from oxidation by the fused chloride of potassium with which it is enveloped. This oxide is also formed by putting tungstic acid in contact with zinc in dilute muriatic acid. The tungstic acid first becomes blue and then assumes a copper colour; but the oxide in this state can with difficulty be preserved, as by exposure to the air, and even under the surface of water, it absorbs oxygen, and is reconverted into tungstic acid.

Oxide of tungsten, when prepared by means of hydrogen gas has a brown colour, and when polished acquires the colour of copper; but when procured by Wöhler's process, it is nearly black. It does not unite, so far as is known, with acids; and when heated to near redness, it takes fire and yields tungstic acid.

*Chlorides of Tungsten.*—According to Wöhler, tungsten and chlorine unite in three proportions. The perchloride is generated by heating the oxide of tungsten in chlorine gas. The action is attended with the appearance of combustion, dense fumes arise, and a thick sublimate is obtained in the form of white scales, like native boracic acid. It is volatile at a low temperature without previous fusion. It is converted by the action of water into tungstic and muriatic acids, and must, therefore, in composition, be proportional to tungstic acid; that is, it consists of 96 parts or one equivalent of tungsten, and 108 parts or three equivalents of chlorine.

When metallic tungsten is heated in chlorine gas, it takes fire, and yields the deutochloride. The compound appears in the form of delicate fine needles, of a deep red colour resembling wool, but more frequently as a deep red fused mass, which has the brilliant fracture of cinnabar. When heated, it fuses, boils, and yields a red vapour. By water, it is changed into muriatic acid and oxide of tungsten. It is entirely dissolved by solution of pure potassa, with disengagement of hydrogen gas, yielding muriate and tungstate of potassa. A similar change is produced by ammonia, except that some oxide of tungsten is left undissolved.

Another chloride has been described by Wöhler. It is formed at

the same time as the first; and though it is converted into muriatic and tungstic acids by the action of water, and would thus seem identical with the perchloride in the proportion of its elements, its other properties are nevertheless different. It is the most beautiful of all these compounds, existing in long transparent crystals of a fine red colour. It is very fusible and volatile, and its vapour is red like that of nitrous acid. The difference between this compound and the chloride first described, has not yet been discovered.

The compounds of tungsten with the other simple substances have been very little or not at all examined.

## *Columbium.*

This metal was discovered in 1801 by Mr Hatchett, who detected it in a black mineral belonging to the British museum, supposed to have come from Massachusetts in North America, and, from this circumstance, applied to it the name of *columbium*. About two years after, M. Ekeberg, a Swedish chemist, extracted the same substance from *tantalite* and *yttro-tantalite;* and, on the supposition of its being different from columbium, described it under the name of *tantalum*. The identity of these metals, however, was established in the year 1809 by Dr Wollaston.

Columbic acid is with difficulty reduced to the metallic state by the action of heat and charcoal; but Berzelius succeeded in obtaining this metal by the same process which he employed in the preparation of zirconium and silicium, namely, by heating potassium with the double fluoride of potassium and columbium. (*Lehrbuch der Chemie*, ii. 120.) On washing the reduced mass with hot water, in order to remove the fluoride of potassium, columbium is left in the form of a black powder. In this state it does not conduct electricity; but in a denser state it is a perfect conductor. By pressure it acquires metallic lustre, and has an iron gray colour. It is not fusible at the temperature at which glass is fused. When heated in the open air, it takes fire considerably below the temperature of ignition, and glows with a vivid light, yielding columbic acid. It is scarcely at all acted on by the sulphuric, muriatic, or nitro-muriatic acid; whereas it is dissolved with heat and disengagement of hydrogen gas by hydrofluoric acid, and still more easily by a mixture of nitric and hydrofluoric acids. It is also converted into columbic acid by fusion with hydrate of potassa, the hydrogen gas of the water being evolved.

Columbium unites with oxygen in two proportions, giving rise to an oxide and an acid. The oxygen in these compounds is in the ratio of 2 to 3; and the experiments of Berzelius lead to the inference that the oxide is formed of 185 parts or one equivalent of columbium, united with 16 parts or two equivalents of oxygen, and the acid, of one equivalent of the metal to three of oxygen. But the combining proportion of the acid is not known with such certainty as altogether to establish the accuracy of this opinion.

The oxide of columbium is generated by placing columbic acid in a crucible lined with charcoal, luting carefully to exclude atmospheric air, and exposing it for an hour and a half to intense heat. The acid, where in direct contact with charcoal, is entirely reduced; but the film of metal is very thin. The interior portions are pure oxide of a dark-gray colour, very hard and coherent. When reduced to powder, its colour is dark brown. It is not attacked by any acid, even by nitro-hydrofluoric acid; but it is converted into columbic acid either

by fusion with hydrate of potassa, or deflagration with nitre. When heated to low redness, it takes fire, and glows, yielding a light gray powder; but in this way it is never completely oxidized. Berzelius states that this oxide, in union with protoxide of iron and a little protoxide of manganese, occurs at Kimito in Finland, and may be distinguished from the other ores of columbium by yielding a chesnut-brown powder.

Columbium exists in most of its ores as an acid, united either with the oxides of iron and manganese, as in tantalite, or with the earth yttria, as in the yttro-tantalite. This acid is obtained by fusing its ore with three or four times its weight of carbonate of potassa, when a soluble columbate of that alkali results, from which columbic acid is precipitated as a white hydrate by acids. Berzelius also prepares it by fusion with bisulphate of potassa.

The hydrated columbic acid is tasteless, and insoluble in water; but when placed on moistened litmus paper, it communicates a red tinge. It is dissolved by the sulphuric, muriatic, and some vegetable acids; but it does not diminish their acidity, or appear to form definite compounds with them. With alkalies it unites readily; and though it does not neutralize their properties completely, crystallized salts may be obtained by evaporation. When the hydrated acid is heated to redness, water is expelled, and the anhydrous columbic acid remains. In this state it is attacked by alkalies only.

*Chloride of Columbium.*—When columbium is heated in chlorine gas, it takes fire and burns actively, yielding a yellow vapour, which condenses in the cold parts of the apparatus in the form of a white powder with a tint of yellow. Its texture is not in the least crystalline. By contact with water, it is converted, with a hissing noise and increase of temperature, into columbic and muriatic acids.

*Sulphuret of Columbium.*—This compound, first prepared by Rose, is generated, with the phenomena of combustion, when columbium is heated to commencing redness in the vapour of sulphur; or by transmitting the vapour of sulphuret of carbon over columbic acid in a porcelain tube at a white heat, carbonic oxide being also evolved.

Berzelius has also described a compound of columbium and fluorine. The other compounds of columbium have been scarcely or not at all examined.

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## SECTION XVII.

### *ANTIMONY.*

Antimony sometimes occurs native; but its only ore which is abundant, and from which the antimony of commerce is derived, is the sulphuret. This sulphuret was long regarded as the metal itself, and was called *antimony*, or *crude antimony;* while the pure metal was termed the *regulus* of *antimony*.

Metallic antimony may be obtained either by heating the native sulphuret in a covered crucible with half its weight of iron filings; or by mixing it with two-thirds of its weight of cream of tartar and one-third of nitre, and throwing the mixture, in small successive portions, into a red-hot crucible. By the first process, the sulphur unites with iron, and in the second, it is expelled in the form of sulphurous acid;

while the fused antimony, which in both cases collects at the bottom of the crucible, may be drawn off and received in moulds. The antimony, thus obtained, is not absolutely pure; and therefore, for chemical purposes, should be procured by heating the oxide with an equal weight of cream of tartar.

Antimony is a brittle metal, of a white colour running into bluish-gray, and is possessed of considerable lustre. Its density is about 6.7. At 810° F. it fuses; and when slowly cooled, sometimes crystallizes in octahedral or dodecahedral crystals. Its structure is highly lamellated. It has the character of being a volatile metal; but Thenard found that it bears an intense white heat without subliming, provided atmospheric air be perfectly excluded, and no gaseous matters, such as carbonic acid or watery vapour, be disengaged during the process. Its surface tarnishes by exposure to the atmosphere; and by the continued action of air and moisture, a dark matter is formed which Berzelius regards as a definite compound. It appears, however, to be merely a mixture of the real protoxide and metallic antimony. Heated to a white or even full red heat in a covered crucible, and then suddenly exposed to the air, it inflames, and burns with a white light.

During the combustion a white vapour rises, which condenses on cool surfaces, frequently in the form of small shining needles of silvery whiteness. These crystals were formerly called *argentine flowers of antimony*, and in chemical works are generally described as the deutoxide of antimony; but according to Berzelius they are a protoxide, an opinion which I believe to be correct.

The chemists who have paid most attention to the oxides of antimony are Thenard*, Proust†, Berzelius‡, and Thomson§. The former maintained the existence of six, the second of two, the third of four, and the last of three oxides of antimony. The opinion of Dr Thomson is now admitted by most chemists; and there is reason to believe that the proportions which he has assigned to these oxides are very near the truth.

| | *Antimony.* | | *Oxygen.* |
|---|---|---|---|
| Protoxide . | 44 | or one equivalent, | 8 = 52 |
| Deutoxide . | 44 | . . . | 12 = 56 |
| Peroxide . | 44 | . . . | 16 = 60 |

*Protoxide.*—When the muriate of the protoxide of antimony, made by boiling the sulphuret in muriatic acid, (page 243) is poured into water, a white curdy precipitate, formerly called *powder of Algaroth*, subsides, which is a submuriate of the protoxide‖. On digesting this salt in a solution of carbonate of potassa, and then edulcorating it with water, the protoxide is obtained in a state of purity. It may also be procured directly, by adding the carbonate of potassa to a solution of

* An. de Chimie, vol. xxxii. † Journal de Physique, vol. lv.
‡ An. de Chimie, vol. lxxxiii; and An. de Ch. et de Ph. vol. xvii.
§ First Principles, vol. ii.
‖ As there is no instance known of an insoluble muriate, it is not probable that the powder of Algaroth is a submuriate of the protoxide of antimony. Dr Duncan suggests that this preparation is probably Dr Thomson's dichloride of antimony, consisting of one equivalent of chlorine and two equivalents of antimony; but this is not likely, as Dr Thomson states that the dichloride is partially soluble in water. Upon the whole, it seems most probable, that the powder of Algaroth is essentially the protoxide of antimony merely contaminated with a small portion of muriatic acid. B.

tartar emetic. It is also generated during the combustion of metallic antimony; but, as thus formed, I apprehend it is not quite pure.

Protoxide of antimony, when prepared in the moist way, is a white powder with a somewhat dirty appearance. When heated it acquires a yellow tint, and at a dull red heat in close vessels it is fused, yielding a yellow fluid, which becomes an opake grayish crystalline mass on cooling. It is very volatile, and if protected from atmospheric air may be sublimed completely without change. When heated in open vessels, it absorbs oxygen; and when the temperature is suddenly raised, and the oxide is porous, it takes fire and burns. It both cases the deutoxide is generated. It is the only oxide of antimony which forms regular salts with acids, and is the base of the medicinal preparation *tartar emetic*, the tartrate of antimony and potassa. Most of its salts, however, are either insoluble in water, or, like the muriate of antimony, are decomposed by it, owing to the affinity of that fluid for the acid being greater than that of the acid for the oxide of antimony. This oxide is therefore a feeble base; and, indeed, possesses the property of uniting with alkalies. To the foregoing remark, however, the tartrate of antimony and potassa is an exception; for it dissolves readily in water without change. By excess of tartaric or muriatic acid, the insoluble salts of antimony may be rendered soluble in water.

The presence of antimony in solution is easily detected by sulphuretted hydrogen. This gas occasions an orange-coloured precipitate, the hydrated protosulphuret of antimony, which is soluble in pure potassa, and is dissolved with disengagement of sulphuretted hydrogen gas by hot muriatic acid, forming a solution from which the white submuriate is precipitated by water*.

*Deutoxide.* When metallic antimony is digested in strong nitric acid, the metal is oxidized at the expense of the acid, and a white hydrate of the peroxide is formed; and on exposing this substance to a red heat, it gives out water and oxygen gas, and is converted into the deutoxide. It is also generated when the protoxide is exposed to heat in open vessels. Thus, on heating sulphuret of antimony with free exposure to the air, sulphurous acid and protoxide of antimony are generated; but on continuing the roasting until all the sulphur is burned, the protoxide gradually absorbs oxygen and passes into the deutoxide. Hence this oxide is formed in the process for preparing the *pulvis antimonialis* of the pharmacopœia.

The deutoxide of antimony is white, infusible, and fixed in the fire, two characters by which it is readily distinguished from the protoxide. It is insoluble in water, and likewise in acids after being heated to redness. It combines with alkalies, and for this reason it has been called *antimonious acid*, and its salts *antimonites*, by Berzelius. The antimonious acid is precipitated from these salts by acids as a hydrate, which reddens litmus paper, and is dissolved by muriatic and tartaric acids, though without appearing to form with them definite compounds.

The *peroxide* of antimony, or *antimonic acid*, is obtained as a white hydrate, either by digesting the metal in strong nitric acid, or by dissolving it in nitro-muriatic acid, concentrating by heat to expel excess of acid, and throwing the solution into water. When recently precipitated it reddens litmus paper, and may be dissolved in water

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* For an account of the means of detecting antimony in mixed fluids, for the purpose of judicial inquiry, the reader may consult an essay on that subject in the Medical and Surgical Journal for 1827.

by means of muriatic or tartaric acids. It does not enter into definite combination with acids, but with alkalies forms salts, which are called *antimoniates*. When the hydrated peroxide is exposed to a temperature of 500° or 600° F. the water is evolved, and the pure peroxide of a yellow colour remains. In this state it resists the action of muriatic acid. When exposed to a red heat, it parts with oxygen, and is converted into the deutoxide.

*Chlorides of Antimony*. When antimony in powder is thrown into a jar of chlorine gas, combustion ensues, and the protochloride of antimony is generated. The same compound may be formed by distilling a mixture of antimony with about twice and a half its weight of corrosive sublimate, when the volatile chloride of antimony passes over into the recipient, and metallic mercury remains in the retort. At common temperatures it is a soft solid, thence called *butter of antimony*, which is liquefied by gentle heat, and crystallizes on cooling. It deliquesces on exposure to the air; and when mixed with water, is converted into muriatic acid and protoxide of antimony. If a large quantity of water is employed, the whole of the oxide subsides as the submuriate.

The bichloride is generated by passing dry chlorine gas over heated metallic antimony. It is a transparent volatile liquid, which emits fumes on exposure to the air. Mixed with water, it is converted into muriatic acid and the hydrated peroxide, which subsides. It contains twice as much chlorine as the protochloride, or is composed of one equivalent of antimony, and two equivalents of chlorine. (Rose in the Annals of Philosophy, N. S. vol. x.)

Dr Thomson, in his "First Principles," has described another chloride of antimony, composed of one equivalent of chlorine and two equivalents of the metal. It is, therefore, a *dichloride*.

*Sulphurets of Antimony*. The native sulphuret of antimony is of a lead-gray colour, and though generally compact, sometimes occurs in acicular crystals, or in rhombic prisms. When heated in close vessels, it enters into fusion without undergoing any other change. Boiled in hot muriatic acid, it is dissolved with disengagement of sulphuretted hydrogen. The experiments of Berzelius, Dr Davy, and Thomson, leave no doubt of its being analogous in composition to the protoxide of antimony, that is, consisting of one equivalent of each of its elements. It may be formed artificially by fusing together antimony and sulphur, or by transmitting a current of sulphuretted hydrogen gas through a solution of tartar emetic. The orange precipitate, which subsides in the last mentioned process, is commonly regarded as the hydrosulphuret of the oxide of antimony. In my opinion it is a hydrated sulphuret of the metal; for when well washed and treated by sulphuric acid, it does not yield a trace of sulphuretted hydrogen.

When sulphuret of antimony is boiled in a solution of potassa, a liquid is obtained, from which, as it cools, an orange-coloured matter, called *Kermes mineral*, is deposited; and on subsequently neutralizing the cold solution with an acid, an additional quantity of a similar substance, the *golden sulphuret* of the pharmacopœia, subsides. Both these compounds, thus procured, are essentially the same as the hydrated sulphuret above described. The action of the alkali on the sulphuret of antimony admits of a two-fold explanation. It is possible that the latter may be dissolved directly by the former, and that it is again deposited when the alkali is neutralized. It is more probable, however, that the elements of water and the sulphuret of antimony react on one another, forming sulphuretted hydrogen and protoxide of antimony; and that the liquid contains a double salt, composed of one equivalent of potassa, one equivalent of the protoxide of antimony, and

one equivalent of sulphuretted hydrogen. On neutralizing the potassa with an acid, sulphuretted hydrogen and the protoxide are set at liberty, and by mutual reaction of their elements are reconverted into water and protosulphuret of antimony.

The *sesquisulphuret* is formed, according to M. Rose, by transmitting sulphuretted hydrogen gas through a solution of the deutoxide of antimony in dilute muriatic acid. (Annals of Philosophy, N. S. vol. x.)

M. Rose formed the *bisulphuret*, consisting of one equivalent of antimony and two equivalents of sulphur, by the action of sulphuretted hydrogen on a solution of the peroxide. The golden sulphuret, prepared by boiling sulphuret of antimony and sulphur in solution of potassa, a process which is not adopted by either of our Colleges, is a bisulphuret.

M. Rose has likewise demonstrated that the *red antimony* of Mineralogists *(rothspiesglanzerz)* is a compound of one equivalent of the protoxide, combined with two equivalents of the protosulphuret of antimony. The pharmaceutic preparations known by the terms of *glass*, *liver*, and *crocus* of antimony, are of a similar nature, though less definite in composition, owing to the mode by which they are prepared. They are made by roasting the native sulphuret, so as to form sulphurous acid and oxide of antimony, and then vitrifying the oxide together with the undecomposed ore, by means of a strong heat. The product will of course differ according as more or less of the sulphuret escapes oxidation during the process.

## SECTION XVIII.

### *URANIUM. CERIUM. COABLT. NICKEL.*

### *Uranium.*

Uranium was discovered in the year 1789 by Klaproth in a mineral of Saxony, called from its black colour *pitchblende*, which consists of the protoxide of uranium and oxide of iron. From this ore the uranium may be conveniently extracted by the following process.—After heating the mineral to redness, and reducing it to fine powder, it is digested in pure nitric acid diluted with three or four parts of water, taking the precaution to employ a larger quantity of the mineral than the nitric acid present can dissolve. By this mode of operating, the protoxide is converted into the peroxide of uranium, which unites with the nitric acid almost to the total exclusion of the iron. A current of sulphuretted hydrogen gas is then transmitted through the solution, in order to separate lead and copper, the sulphurets of which are always mixed with pitchblende. The solution is boiled to expel the free sulphuretted hydrogen, and, after being concentrated by evaporation, is set aside to crystallize. The nitrate of uranium is gradually deposited in flattened four-sided prisms of a beautiful lemon-yellow colour.

The properties of metallic uranium are as yet known imperfectly. It was prepared by Arfwedson, by conducting hydrogen gas over the protoxide of uranium heated in a glass tube. The substance obtained

by this process was crystalline, of a metallic lustre, and of a reddish-brown colour. It suffered no change on exposure to air at common temperatures; but when heated in open vessels absorbed oxygen, and was reconverted into the protoxide. From its lustre, it was inferred to be metallic uranium.

Chemists are acquainted with two compounds of uranium and oxygen, the composition of which has been minutely studied by Arfwedson* and Thomson†. According to the chemist last mentioned, whose experiments are the most recent, the equivalent of uranium is 208, and its oxides are composed of

| | *Uranium.* | *Oxygen.* |
|---|---|---|
| Protoxide . | 208 . | 8 = 216 |
| Peroxide . | 208 . | 16 = 224 |

According to the analyses of Arfwedson, 216 is the atomic weight of uranium, and the oxygen in its two oxides is in the ratio of 1 to 1.5; and Berzelius, from the composition of three salts of uranium, has arrived at a similar conclusion.

The protoxide of uranium is of a very dark green colour, and is obtained by decomposing the nitrate of the peroxide by heat. It is exceedingly infusible, and bears any temperature hitherto tried without change. It unites with acids, forming salts of a green colour. It is readily oxidized by nitric acid, and yields a yellow solution which is a nitrate of the peroxide. The protoxide is employed in the arts for giving a black colour to porcelain.

The peroxide of uranium is of a yellow or orange colour, and most of its salts have a similar tint. It not only combines with acids, but likewise unites with alkaline bases, a property which was first noticed by Arfwedson. It is precipitated from acids as a yellow hydrate by pure alkalies, fixed or volatile; but retains a portion of these bases in combination. It is thrown down as a carbonate by the carbonate of soda or ammonia, and is redissolved by an excess of the precipitant, a circumstance which affords an easy method of separating uranium from iron. It is not precipitated by sulphuretted hydrogen. With ferrocyanate of potassa it gives a brownish-red precipitate, not unlike the ferrocyanate of the peroxide of copper.

The peroxide of uranium is decomposed by a strong heat, and converted into the protoxide. From its affinity for alkalies, it is difficult to obtain it in a state of perfect purity. It is employed in the arts for giving an orange colour to porcelain.

## *Cerium.*

Cerium was discovered in the year 1803 by MM. Hisinger and Berzelius, in a rare Swedish mineral known by the name of cerite, and its existence was recognised about the same time by Klaproth. Dr Thomson has since found it to the extent of thirty-four per cent in a mineral from Greenland, called *Allanite*, in honour of Mr Allan, who first distinguished it as a distinct species.

The properties of cerium are in a great measure unknown. It appears from the experience of Vauquelin, who obtained it in minute buttons not larger than the head of a pin, that it is a white brittle

* Annals of Philosophy, N. S. vol. vii.
† First Principles, vol. ii.

metal, which resists the action of nitric, but is dissolved by nitro-muriatic acid. According to an experiment made by Mr Children and Dr Thomson, metallic cerium is volatile in very intense degrees of heat. (Annals of Philosophy, vol. ii.)

*Oxides of Cerium.*—Cerium unites with oxygen in two proportions, and the composition of the resulting oxides has been particularly studied by M. Hisinger*. Dr Thomson† has likewise made experiments on the subject, and infers from data furnished partly by himself and partly by M. Hisinger, that 50 is the atomic weight of cerium, and that its oxides are thus constituted:—

| | *Cerium.* | *Oxygen.* | |
|---|---|---|---|
| Protoxide | 50 | 8 | = 58 |
| Deutoxide | 50 | 12 | = 62 |

The protoxide of cerium is a white powder, which is insoluble in water, and forms salts with acids, all of which, if soluble, have an acid reaction. Exposed to the air at common temperatures it suffers no change; but if heated in open vessels, it absorbs oxygen and is converted into the peroxide. It is precipitated from its salts as a white hydrate by pure alkalies; as a white carbonate by alkaline carbonates, but is redissolved by the precipitant in excess; and as a white oxalate by the oxalate of ammonia.

The peroxide of cerium is of a fawn-red colour. It is dissolved by several of the acids, but is a weaker base than the protoxide. Digested in muriatic acid, chlorine is disengaged and a protomuriate results.

The most convenient method of extracting pure oxide of cerium from cerite is by the process of Laugier. After reducing the cerite to powder, it is dissolved in nitro-muriatic acid, and the solution is evaporated to perfect dryness. The soluble parts are then redissolved by water, and an excess of ammonia is added. The precipitate thus formed, consisting of the oxides of iron and cerium, is well washed, and afterwards digested in a solution of oxalic acid, which dissolves the iron, and forms an insoluble oxalate with the cerium. By heating this oxalate to redness in an open fire, the acid is decomposed, and the peroxide of cerium is obtained in a pure state.

*Sulphuret of Cerium.*—Dr Mosander has succeeded in forming this compound by two different processes. The first method is by transmitting the vapour of sulphuret of carbon over carbonate of cerium at a red heat; and the second is by fusing oxide of cerium at a white heat with a large excess of sulphuret of potassium (*hepar sulphuris*) and afterwards removing the soluble parts by water. The product of the first operation is porous, light, and of a red colour like red lead; and that of the second is in small brilliant scales, and of a yellow colour, like *aurum musivum*. These sulphurets, though different in appearance, are similar in point of composition, containing 26 per cent of sulphur. They are insoluble in water, but are dissolved in acids with evolution of sulphuretted hydrogen gas, without any residuum of sulphur. (Philos. Mag. and Annals, i. 71.)

## *Cobalt.*

This metal is met with in the earth chiefly in combination with arsenic, constituting an ore from which all the cobalt of commerce is

* Annals of Philosophy, vol. iv.
† First Principles, vol. i.

derived. It is a constant ingredient of meteoric iron; at least Professor Stromeyer informs me that he has analysed several varieties, in every one of which he has detected the presence of cobalt.

When the native arseniuret of cobalt is broken into small pieces, and exposed in a reverberatory furnace to the united action of heat and air, its elements are oxidized, most of the arsenious acid is expelled in the form of vapour, and an impure oxide of cobalt, called *zaffre*, remains. On heating this substance with a mixture of sand and potassa, a beautiful blue coloured glass is obtained, which, when reduced to powder, is known by the name of *smalt*.

Metallic cobalt may be obtained by dissolving zaffre in muriatic acid, and transmitting through the solution a current of sulphuretted hydrogen gas, until the arsenious acid is completely separated in the form of sulphuret of arsenic. The filtered liquid is then boiled with a little nitric acid, in order to convert the protoxide into the peroxide of iron, and an excess of the carbonate of potassa is added. The precipitate, consisting of the peroxide of iron and carbonate of cobalt, after being well washed with water, is digested in a solution of oxalic acid, which dissolves the iron and leaves the cobalt in the form of an insoluble oxalate. (Laugier.) On heating the oxalate of cobalt in a retort from which the atmospheric air is excluded, a large quantity of carbonic acid is evolved, and a black powder, metallic cobalt, is left. (Thomson in Annals of Philosophy, N.S. i.) The pure metal is easily procured also by passing a current of dry hydrogen gas over the oxide of cobalt heated to redness in a tube of porcelain.

Cobalt is a brittle metal, of a reddish-gray colour, and weak metallic lustre. Its density is 8.538. It fuses at about 130° of Wedgwood, and when slowly cooled it crystallizes. It is attracted by the magnet, and is susceptible of being rendered permanently magnetic. It undergoes little change in the air, but absorbs oxygen when heated in open vessels. It is attacked with difficulty by sulphuric or muriatic acid, but is readily oxidized by means of nitric acid.

*Oxides of Cobalt.*—Chemists are acquainted with two oxides of cobalt. According to the experiments of Rothoff*, the protoxide is composed of 29.5 parts of cobalt and 8 parts of oxygen, so that the atomic weight of cobalt is 29.5. Dr Thomson, on the contrary, infers from his analysis of the sulphate of cobalt, that 26 is the equivalent of this metal. From this discordance it may be doubted if the atomic weight of cobalt is known with certainty. According to Rothoff, the oxygen contained in the two oxides is as 1 to 1.5.

The protoxide is of an ash-gray colour, and is the basis of the salts of cobalt, most of which are of a pink hue. When heated to redness in open vessels it absorbs oxygen, and is converted into the peroxide. It may be prepared by decomposing carbonate of cobalt by heat in a vessel from which the atmospheric air is excluded. It is easily recognised by giving a blue tint to borax when melted with it; and is employed in the arts, in the form of smalt, for communicating a similar colour to glass, earthenware, and porcelain.

The protoxide of cobalt is precipitated from its salts by pure potassa as a blue hydrate, which absorbs oxygen from the air, and gradually becomes black. Pure ammonia likewise causes a blue precipitate, which is redissolved by the alkali if in excess. It is thrown down as a pale pink carbonate by the carbonate of potassa, soda, or ammonia; but an excess of the last redissolves it with facility. Sulphuretted hy-

* Annals of Philosophy, vol. iii. p. 356.

drogen produces no change, unless the solution is quite neutral, or the oxide is combined with a weak acid. Alkaline hydrosulphurets always precipitate it as the black sulphuret of cobalt.

The muriate of cobalt is celebrated as a sympathetic ink. When diluted with water so as to form a pale pink solution, and then employed as ink, the letters, which are invisible in the cold, become blue if gently heated.

The peroxide of cobalt is of a black colour, and is easily formed from the protoxide in the way already mentioned. It does not unite with acids; and when digested in muriatic acid, the protomuriate of cobalt is generated with disengagement of chlorine. When strongly heated in close vessels, it gives off oxygen, and is converted into the protoxide.

The compounds of cobalt with the other non-metallic bodies have hitherto been little examined.

## *Nickel.*

Nickel is a constituent of meteoric iron. It occurs likewise in the copper-coloured mineral of Westphalia, termed *copper-nickel*, a native arseniuret of nickel, which, in addition to its chief constituents, contains sulphur, iron, cobalt, and copper. The preparations of nickel may either be made from this mineral or from the artificial arseniuret called *speiss*, a metallurgic production obtained in forming smalt from the roasted ores of cobalt. Various processes have been devised for procuring a pure salt of nickel, but the following appears to me as simple and perhaps as successful as any. After reducing speiss to fine powder, it is digested in sulphuric acid, to which a fourth part of nitric acid is added; and when the solution is saturated with nickel, it is set aside for several hours in order that arsenious acid may separate, and then filtered. The clear liquid is subsequently mixed with a solution of sulphate of potassa, and set aside to crystallize spontaneously; when a double salt, the sulphate of nickel and potassa, is deposited. Dr Thomson, who proposed this process, states that the crystals thus obtained are quite free from arsenic and iron, and contain no impurities except copper and cobalt. The former is easily precipitated as sulphuret by a current of sulphuretted hydrogen gas, a little free sulphuric acid being previously added; and at the same time any traces of arsenic, if present, would likewise subside as orpiment. The filtered liquid is then heated to expel free sulphuretted hydrogen, and the oxides of nickel and cobalt precipitated by carbonate of potassa. The separation of these oxides may then be effected by the method suggested by M. Berthier. The mixed hydrates, after being well washed, are suspended in water through which chlorine is transmitted to saturation. All the cobalt, and generally some nickel, is converted into peroxide and thus rendered insoluble; while the greater part of the nickel is dissolved in the form of muriate, and may be removed from the insoluble peroxides by filtration.

Metallic nickel, which may be prepared either by heating the oxalate in close vessels, or by the combined action of heat and charcoal or hydrogen on the oxide of nickel, is of a white colour, intermediate between that of tin and silver. It has a strong metallic lustre, and is both ductile and malleable. It is attracted by the magnet, and like iron and cobalt may be rendered magnetic. Its specific gravity after fusion is about 8.279, and is increased to near 9.0 by hammering.

Nickel is exceedingly infusible, even more so than pure iron. It suffers no change at common temperatures by exposure to air and

moisture; but it absorbs oxygen at a red heat, though not rapidly, and is partially oxidized. The muriatic and sulphuric acids act upon it with difficulty. By the nitric acid, it is readily oxidized, and forms a nitrate of the protoxide of nickel.

Nickel is susceptible of two stages of oxidation. According to the experiments of Berzelius, Berthier, and Thomson, the combining proportion of nickel is 26, and that of its protoxide 34. The protoxide may hence be regarded as a compound of one equivalent of each element. (Edinburgh Journal of Science, No. xiii. 157.) The peroxide of nickel has been less fully examined than the protoxide; but from some experiments of Rothoff, it appears to consist of 26 parts or one equivalent of nickel, and 12 parts or one equivalent and a half of oxygen.

The protoxide of nickel may be formed by heating the carbonate, oxalate, or nitrate to redness in an open vessel, and is then of an ash-gray colour; but after being heated to whiteness, its colour is a dull olive-green. It is not attracted by the magnet. It is a strong alkaline base, and nearly all its salts have a green tint. It is precipitated as a hydrate of a pale green colour by the pure alkalies, but is redissolved by ammonia in excess; as a pale green carbonate by alkaline carbonates, but is dissolved by an excess of the carbonate of ammonia; and as a black sulphuret by alkaline hydrosulphurets. Sulphuretted hydrogen occasions no precipitate, unless the solution is quite neutral, or the oxide combined with a weak acid.

The peroxide of nickel is of a black colour, and is formed by transmitting chlorine gas through water, in which the hydrate of the protoxide is suspended. The peroxide of nickel does not unite with acids, is decomposed by a red heat, and with hot muriatic acid forms a proto-muriate with disengagement of chlorine gas.

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# SECTION XIX.

## *BISMUTH. TITANIUM. TELLURIUM.*

### *Bismuth.*

Bismuth is found in the earth both native and in combination with other substances, such as sulphur, oxygen, and arsenic. That which is employed in the arts is derived chiefly from native bismuth, and commonly contains small quantities of sulphur, iron, and copper. It may be obtained pure for chemical purposes by heating the oxide or subnitrate to redness along with charcoal.

Bismuth has a reddish-white colour and considerable lustre. Its structure is highly lamellated, and when slowly cooled, it crystallizes in octahedrons. Its density is about 10. It is brittle when cold, but may be hammered into plates while warm. At 476° F. it fuses, and sublimes in close vessels at about 30° of Wedgwood. It is a less perfect conductor of caloric than most other metals.

Bismuth undergoes little change by exposure to air at common temperatures. When fused in open vessels, its surface becomes covered with a gray film, which is a mixture of metallic bismuth with the oxide of the metal. Heated to its subliming point, it burns with a bluish-

white flame, and emits copious fumes of the oxide of bismuth. The metal is attacked with difficulty by muriatic or sulphuric acid, but it is readily oxidized and dissolved by nitric acid.

*Oxide of Bismuth.*—This metal unites with oxygen in one proportion only, forming a yellow-coloured oxide, which may be easily procured by heating the subnitrate to redness. At a full red heat it is fused, and yields a transparent yellow glass. At a still higher temperature it is sublimed. It unites with acids, and most of its salts are white. According to the experiments of Dr J. Davy*, it is composed of 72 parts of bismuth, and 8 parts of oxygen, and therefore 72 is the atomic weight of bismuth, and 80 the equivalent of its oxide. This result is confirmed by the researches of Dr Thomson†.

When the nitrate of bismuth, either in solution or in crystals, is put into water, a copious precipitate, the subnitrate, of a beautifully white colour subsides, which was formerly called the *magistery of bismuth*. From its whiteness, it is sometimes employed as a paint for improving the complexion; but it is an inconvenient pigment, owing to the facility with which it is blackened by sulphuretted hydrogen. If the nitrate with which it is made contains no excess of acid, and a large quantity of water is employed, the whole of the bismuth is separated as a subnitrate. By this character bismuth may be both distinguished and separated from other metals.

*Chloride of Bismuth.*—When bismuth in fine powder is introduced into chlorine gas, it takes fire, burns with a pale blue light, and is converted into a chloride, formerly termed *butter* of bismuth. It may be prepared conveniently by heating two parts of corrosive sublimate with one of bismuth, and afterwards expelling the excess of the former, together with the metallic mercury, by heat.

The chloride of bismuth is of a grayish-white colour, opake, and of a granular texture. It fuses at a temperature a little above that at which the metal itself is liquefied, and bears a red heat in close vessels without subliming. (Dr Davy.) From the experiments of Drs Davy and Thomson, it appears to consist of one equivalent of each of its elements.

*Sulphuret of Bismuth.*—This sulphuret is found native, and may be formed artificially by fusing bismuth with sulphur. It is of a lead-gray colour, and metallic lustre. The experiments of Dr Davy, Thomson, and Lagerhielm‡ leave no doubt of its being composed of one equivalent of bismuth and one equivalent of sulphur. I apprehend the dark brown precipitate caused by the action of sulphuretted hydrogen on the salts of bismuth is likewise a protosulphuret.

## *Titanium.*

Titanium was first recognised as a new substance by Mr Gregor of Cornwall, and its existence was afterwards established by Klaproth.§ But the properties of the metal were not ascertained in a satisfactory manner until the year 1822, when Dr Wollaston|| was led to examine some minute crystals which were found in a slag at the bottom of a smelting furnace at the great iron works at Merthyr Tydvil in Wales, and presented to him by Mr Buckland. These crystals, which have since been found at other iron works, are of a cubic form, and in

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* Philosophical Transactions for 1812. † First Principles, vol. i.
‡ Annals of Philosophy, vol. iv. § Contributions, vol. i.
|| Philosophical Transactions for the year 1823.

colour and lustre are like burnished copper. They conduct electricity, and are attracted slightly by the magnet, a property which seems owing to the presence of a minute quantity of iron. Their specific gravity is 5.3; and their hardness so great, that they scratch a polished surface of rock crystal. They are exceedingly infusible; but when exposed to the united action of heat and air, their surface becomes covered with a purple coloured film which is an oxide. They resist the action of nitric and nitro-muriatic acids, but are completely oxidized by being strongly heated with nitre. They are then converted into a white substance, which possesses all the properties of the peroxide of titanium. By this character they are proved to be metallic titanium.

*Oxides of Titanium.*—This metal has probably two degrees of oxidation. The *protoxide* is of a purple colour, and is supposed to exist pure in the mineral called *anatase*; but its composition and chemical properties are unknown. The *peroxide* exists in a nearly pure state in the titanite or rutile. The menaccanite, in which titanium was originally discovered by Mr Gregor, is a compound of the oxides of titanium, iron, and manganese. This oxide is best prepared from rutile. The mineral, after being reduced to an exceedingly fine powder, is fused in a platinum crucible with three times its weight of carbonate of potassa, and the mass afterwards washed with water to remove the excess of alkali. A gray mass remains, which consists of potassa and oxide of titanium. This compound is dissolved in concentrated muriatic acid; and, on diluting with water, and boiling the solution, the greater part of the oxide of titanium is thrown down. It is then collected on a filter, and well washed with water acidulated with muriatic acid. In this state, the oxide is not quite pure; but contains a little oxide of manganese and iron, derived from the rutile. The best mode of separating these impurities, is to digest the precipitate, while still moist, with hydrosulphuret of ammonia, which converts the oxides of iron and manganese into sulphurets, but does not act on the oxide of titanium. The two sulphurets are readily dissolved by dilute muriatic acid; and the oxide of titanium, after being collected on a filter and well washed, as before, may be dried and heated to redness. This method was proposed by Professor Rose of Berlin. (An. de Ch. et de Physique, xxiii.)

The peroxide of titanium, when pure, is quite white. It is exceedingly infusible and difficult of reduction; and after being once ignited, ceases to be soluble in acids. M. Rose has observed that, like silica, it possesses weak acid properties. Thus he finds that it unites readily with alkalies, and denies its power of acting as an alkaline base. On this account he proposes for it the name of *titanic acid*. In the state of hydrate, as when precipitated from muriatic acid by boiling, or when combined with an alkali after fusion, it has a singular tendency to pass through the pores of a filter when washed with pure water; but the presence of a little acid, alkali, or a salt, prevents this inconvenience. After exposure to a red heat, it is not attacked by acids, except by the hydrofluoric.

If previously ignited with carbonate of potassa, the oxide of titanium is soluble in dilute muriatic acid; but it is retained in solution by so feeble an attraction, that it is precipitated merely by boiling. It is likewise thrown down by the pure and carbonated alkalies, both fixed and volatile. A solution of gall-nuts causes an orange-red colour, which is very characteristic of the presence of titanium. When a rod of zinc is suspended in the solution, a purple-coloured powder, probably the protoxide, is precipitated, which is gradually reconverted into the peroxide.

The atomic weight of titanium, as deduced by Dr Thomson from experiments made by M. Rose and by himself, is 32. Titanic acid is inferred, from the same data, to be composed of 32 parts, or one equivalent of titanium, and 16 parts or two equivalents of oxygen. The combining proportion of the peroxide of titanium, and its chemical constitution, have not, however, been ascertained with certainty.

*Chloride of Titanium.*—This substance was first prepared in the year 1824 by Mr George of Leeds, by transmitting dry chlorine gas over metallic titanium at a red heat. At common temperatures, it is a transparent colourless fluid of considerable specific gravity, boils violently at a temperature a little above 212° F. and condenses again without change. In open vessels, it is attacked by the moisture of the atmosphere, and emits dense white fumes of a pungent odour similar to that of chlorine, but not so offensive. On adding a few drops of water to a few drops of the liquid, a very rapid, almost explosive, disengagement of chlorine gas ensues, attended with considerable increase of temperature; and if the water is not in excess, a solid residue is obtained. This substance is deliquescent, soluble in water, and its solution possesses all the characters of muriate of titanium.

The composition of this chloride has not been satisfactorily established; but it contains more chlorine than is capable of uniting with the hydrogen derived from water, when the oxygen of that fluid converts titanium into the peroxide.

*Sulphuret of Titanium.*—This compound was discovered by Rose, who prepared it by transmitting the vapour of sulphuret of carbon over the peroxide of titanium, heated to whiteness in a tube of porcelain. It occurs in thick green masses, which by the least friction acquire a dark yellow colour and metallic lustre. When heated in the open air, it is converted into sulphurous acid and oxide of titanium. By acids it is slowly decomposed, and is dissolved by muriatic acid with disengagement of sulphuretted hydrogen gas. According to the experiments of Rose, it is proportional to the peroxide of titanium, consisting of 32 parts or one equivalent of titanium, and 32 parts or two equivalents of sulphur.

## *Tellurium.*

Tellurium is a rare metal, hitherto found only in the gold mines of Transylvania, and even there in very small quantity. Its existence was inferred by Müller in the year 1782, and fully established in 1798 by Klaproth.* It occurs in the metallic state, chiefly in combination with gold and silver.

Tellurium has a tin-white colour running into lead-gray, a strong metallic lustre, and lamellated texture. It is very brittle, and its density is 6.115. It fuses at a temperature below redness, and at a red heat is volatile. When heated before the blowpipe, it takes fire, burns rapidly with a blue flame bordered with green, and is dissipated in gray-coloured pungent inodorous fumes. The odour of decayed horse-radish is sometimes emitted during the combustion, and was thought by Klaproth to be peculiar to tellurium; but Berzelius ascribes it solely to the presence of selenium.

*Oxide of Tellurium.*—Tellurium is rapidly oxidized by nitric acid,

* Contributions, vol. iii.

and a soluble nitrate of the oxide results. The oxide is likewise formed during the combustion of the metal. It is of a gray colour, fuses at a red heat, and at a temperature still higher sublimes. When heated before the blowpipe on charcoal, it is decomposed with violence. It has the property of forming salts both with acids and alkalies. It is precipitated from its solution in acids, as a hydrate, by all the alkalies both pure and carbonated; but it is redissolved by an excess of the precipitant. Alkaline hydrosulphurets occasion a black precipitate, which is probably a sulphuret of tellurium. It is reduced to the metallic state, and thrown down as a black powder, by insertion of a rod of zinc, tin, antimony, or iron.

According to Berzelius, the oxide of tellurium is composed of nearly 32 parts of the metal, and 8 parts of oxygen; so that 32 may be regarded as the atomic weight of tellurium, and 40 of its oxide. This result, however, differs considerably from that of Klaproth, and, therefore, requires confirmation.

Tellurium unites in one proportion with chlorine, and in two proportions with hydrogen. The most interesting of these compounds is the telluretted hydrogen gas discovered in the year 1809 by Sir H. Davy. This gas is colourless, has an odour similar to that of sulphuretted hydrogen, and is absorbed by water, forming a claret-coloured solution. As it unites with alkalies, it may be regarded as a feeble acid. It reddens litmus paper at first; but loses this property after being washed with water.

## SECTION XX.

### COPPER.

Native copper is by no means uncommon. It occurs in large amorphous masses in some parts of America, and is sometimes found in octahedral crystals, or in forms allied to the octahedron. The metallic copper of commerce is extracted chiefly from the native sulphuret.

Copper is distinguished from all other metals, titanium excepted, by having a red colour. It receives a considerable lustre by polishing. Its density is 8.78, and is increased by hammering. It is both ductile and malleable, and in tenacity is inferior only to iron. It is hard and elastic, and consequently sonorous. In fusibility it stands between silver and gold.

Copper undergoes little change in a perfectly dry atmosphere, but is rusted in a short time by exposure to air and moisture, being converted into a green substance, the carbonate of the peroxide of copper. At a red heat it absorbs oxygen, and is converted into the peroxide, which appears in the form of black scales. It is attacked with difficulty by muriatic and sulphuric acids, and not at all by the vegetable acids, if atmospheric air be excluded; but if air has free access, the metal absorbs oxygen with rapidity, the attraction of the acid for the oxide of copper co-operating with that of the copper for oxygen. Nitric acid acts with violence on copper, forming a nitrate of the peroxide.

*Oxides of Copper*.—The oxides of this metal have been studied by Proust, Chenevix, Dr Davy, and Berzelius, and especially by the

former*. From the labours of these chemists, it appears that there are but two oxides of copper, and that they are thus constituted:—

| | Copper. | | Oxygen. | | |
|---|---|---|---|---|---|
| Protoxide . | 64 | . | 8 | = | 72 |
| Peroxide . | 64 | . | 16 | = | 80 |

Consequently, if the first be regarded as a compound of one equivalent of each element, 64 is the atomic weight of copper.

The *red* or *protoxide* occurs native in the form of octahedral crystals, and is found of peculiar beauty in the mines of Cornwall. It may be prepared artificially by mixing 64 parts of metallic copper, in a state of fine division, with 80 parts of the peroxide, and heating the mixture to redness in a close vessel; or by boiling a solution of the acetate of copper with sugar, when the peroxide is partially deoxidized, and subsides as a red powder.

The protoxide of copper combines with the muriatic, sulphuric, and probably with several other acids, forming salts, most of which are colourless, and from which the protoxide is precipitated as an orange-coloured hydrate by alkalies. They attract oxygen rapidly from the atmosphere, by which they are converted into per-salts. The proto-muriate is easily formed by putting a solution of the permuriate with free muriatic acid and copper filings into a well closed glass phial. The protoxide of copper is soluble in ammonia, and the solution is quite colourless. It becomes blue, however, with surprising rapidity by free exposure to air, owing to the formation of the peroxide.

The *peroxide* of copper, the *copper black* of mineralogists, is sometimes found native, being formed by the spontaneous oxidation of other ores of copper. It may be prepared artificially by calcining metallic copper, by precipitation from the per-salts of copper by means of pure potassa, and by heating the nitrate of copper to redness.

The peroxide of copper varies in colour from a dark brown to a bluish-black, according to the mode of formation. It undergoes no change by heat alone, but is readily reduced to the metallic state by heat and combustible matter. It is insoluble in water, and does not affect the vegetable blue colours. It combines with nearly all the acids, and most of its salts have a green or blue tint. It is soluble likewise in ammonia, forming with it a deep blue solution, a property by which the peroxide of copper is distinguished from all other substances.

The peroxide of copper is precipitated by pure potassa as a blue hydrate, which is rendered black by boiling, the hydrate being decomposed at that temperature. Pure ammonia at first throws down a greenish-blue insoluble subsulphate†, which is redissolved by the precipitant in excess, and forms the deep blue ammoniacal sulphate of copper. Alkaline carbonates cause a bluish-green precipitate, the carbonate of copper, which is redissolved by an excess of carbonate of ammonia. It is precipitated as a dark brown bisulphuret by sulphuretted hydrogen, and as a reddish-brown ferrocyanate by the ferrocyanate of potassa. The oxide of copper is thrown down of a yellow-

* Journal de Phsyque, vol. lix.

† Dr Turner has taken it for granted here, that the ammonia is added to a solution of the sulphate of copper. The sentence, to make it intelligible to the student, ought to read thus: "From the sulphate of copper, pure ammonia at first throws down," &c. B.

ish-white colour by albumen, and M. Orfila has proved that this compound is inert, so that albumen is an antidote to poisoning by copper.

Copper is separated in the metallic state by a rod of iron or zinc. The copper, thus obtained, after being washed with a dilute solution of muriatic acid, is chemically pure.

The best mode of detecting copper, when supposed to be present in mixed fluids, is by sulphuretted hydrogen. The sulphuret, after being collected, should be placed on a piece of porcelain, and digested in a few drops of nitric acid. A sulphate of copper is formed, which, when evaporated to dryness, strikes the characteristic deep blue on the addition of ammonia.

The red oxide of copper is by some chemists supposed to be a sub-oxide, or a compound of two atoms of copper and one atom of oxygen; while the elements of the black oxide are thought to be in the ratio of one atom of each. According to this view the atomic weight of copper is 32 or half that above stated. This opinion, which is adopted by Dr Thomson, is certainly supported by the tendency of the red oxide to absorb oxygen and pass into the state of black oxide; and other arguments may be adduced in its favour. But, nevertheless, as the red oxide is unquestionably a definite compound, capable of uniting with acids, and proportional to several other compounds, such as the protosulphuret and protochloride of copper, it appears to me more consistent to consider it as the real protoxide, composed of one atom of each of its elements.

*Chlorides of Copper.*—The chlorides of copper have been minutely studied by Proust and Dr Davy. From the able researches of these chemists, and especially of the latter, there is no doubt that the two chlorides are proportional to the two oxides of copper, or that they are composed of

| | *Copper.* | *Chlorine.* |
|---|---|---|
| Protochloride . | 64 . | 36 |
| Perchloride . | 64 . | 72 |

When copper filings are introduced into an atmosphere of chlorine gas, the metal takes fire spontaneously, and both the chlorides are generated.

The *protochloride* may be conveniently prepared by heating copper filings with twice their weight of corrosive sublimate. In this way it was originally made by Mr Boyle, who termed it *resin of copper*, from its resemblance to common resin. Proust procured it by the action of the protomuriate of tin on the permuriate of copper; and also by decomposing the permuriate by heat. He gave it the name of *white muriate of copper*.

The protochloride of copper is fusible at a heat just below redness, and bears a red heat in close vessels without subliming. It is insoluble in water, but dissolves in muriatic acid, and is precipitated unchanged by water as a white powder. Its colour varies with the mode of preparation, being white, yellow, or dark brown.

The *perchloride* is best formed by exposing the permuriate of copper to a temperature not exceeding 400° F. (Dr Davy.) It is a pulverulent substance of a yellow colour, deliquesces on exposure to air, and is reconverted by water into the permuriate. It parts with half its chlorine when strongly heated, and the protochloride of copper is generated.

*Sulphurets of Copper.*—The protosulphuret of copper is a natural production, well known to mineralogists under the name of *copper glance*; and in combination with sulphuret of iron, it is a constituent

of the variegated copper ore. It is formed artificially by heating copper filings with a third of their weight of sulphur. The combination is attended with such free disengagement of caloric, that the mass becomes vividly luminous. According to the analysis of Berzelius, it is composed of 64 parts or one equivalent of copper, and 16 parts or one equivalent of sulphur.

Bisulphuret of copper is a constituent of copper pyrites, in which it is combined with protosulphuret of iron. It may be formed artificially by the action of sulphuretted hydrogen on a per-salt of copper. When exposed to a red heat in a close vessel, it loses half its sulphur, and is converted into the protosulphuret.

The compounds of copper with the other non-metallic bodies are of minor interest, and have hitherto been little studied.

## SECTION XXI.

### *LEAD.*

Native lead is an exceedingly rare production; but in combination, especially with sulphur, it occurs in large quantity. All the metallic lead of commerce is extracted from the native sulphuret, the *galena* of mineralogists.

Lead has a bluish-gray colour, and when recently cut, a strong metallic lustre; but it soon tarnishes by exposure to the air. Its density is 11.358. It is soft, flexible, and inelastic. It is both malleable and ductile, possessing the former property in particular to a considerable extent. In tenacity, it is inferior to all ductile metals. It fuses at about 612° F., and when slowly cooled forms octahedral crystals. It may be heated to whiteness in close vessels without subliming. Most of the compounds of lead are poisonous.

Lead absorbs oxygen quickly at high temperatures. When fused in open vessels, a gray film is formed upon its surface, which is a mixture of metallic lead and protoxide; and when strongly heated, it is dissipated in fumes of the yellow oxide of lead. In pure water, it is oxidized with considerable rapidity, yielding minute shining, brilliantly white, crystalline scales of carbonate of lead, the oxygen and carbonic acid being derived from the atmosphere. The presence of saline matter in water retards the oxidation of the lead; and some salts, even in exceedingly minute quantity, prevent it altogether. Many kinds of spring water, owing to the salts which they contain, do not corrode lead; and hence, though intended for drinking, may be safely collected in leaden cisterns. Of this, the water of Edinburgh is a remarkable instance. Dr Christison is at present occupied with an experimental inquiry on this subject, and has already collected a variety of interesting facts.

Lead is not attacked by the muriatic or the vegetable acids, though their presence, at least in some instances, accelerates the absorption of oxygen from the atmosphere in the same manner as with copper. Cold sulphuric acid does not act upon it; but when boiled in that liquid, the lead is slowly oxidized at the expense of the acid. The only proper solvent for lead is the nitric acid. This reagent oxidizes it rapidly, and forms with its oxide a salt which crystallizes in opake octahedrons by evaporation.

*Oxides of Lead.*—Lead has three degrees of oxidation, and the composition of its oxides, as deterimined with great care by Berzelius,* is as follows:—

| | *Lead.* | *Oxygen.* | |
|---|---|---|---|
| Protoxide | 104 | 8 | = 112 |
| Deutoxide | 104 | 12 | = 116 |
| Peroxide | 104 | 16 | = 120 |

*Protoxide.*—This oxide is prepared on a large scale, by collecting the gray film which forms on the surface of melted lead, and exposing it to heat and air until it acquires a uniform yellow colour. In this state, it is the *massicot* of commerce; and when partially fused by heat, the term *litharge* is applied to it. As thus procured, it is always mixed with the deutoxide. It may be obtained pure by heating the carbonate or nitrate to low redness in a vessel from which atmospheric air is excluded.

The protoxide of lead has a yellow colour, is insoluble in water, fuses at a red heat, and in close vessels is fixed and unchangeable in the fire. Heated with combustible matters, it parts with oxygen and is reduced. From its insolubility, it does not change the vegetable colours under common circumstances; but when rendered soluble by a small quantity of acetic acid, it has a distinct alkaline reaction. It unites with acids, and is the base of all the salts of lead. Most of its salts are of a white colour.

The protoxide of lead is precipitated from its solutions by pure alkalies as a white hydrate, which is redissolved by potassa in excess; as a white carbonate, which is the well-known pigment *white lead*, by alkaline carbonates; as a white sulphate by soluble sulphates; as a dark brown sulphuret by sulphuretted hydrogen; and as the yellow iodide of lead by hydriodic acid or hydriodate of potassa.

M. Orfila has proved experimentally that the sulphate of lead, owing to its insolubility, is not poisonous; and, therefore, the sulphate of magnesia, or any soluble sulphate, renders the active salts of lead inert.

The best method of detecting the presence of lead in wine, or other suspected mixed fluids, is by means of sulphuretted hydrogen. The sulphuret of lead, after being collected on a filter and washed, is to be digested in nitric acid diluted with twice its weight of water, until the dark colour of the sulphuret disappears. The solution of the nitrate of lead should then be brought to perfect dryness on a watch glass, in order to expel the excess of nitric acid, and the residue redissolved in a small quantity of cold water. On dropping a particle of the hydriodate of potassa into a portion of this liquid, the yellow iodide of lead will instantly appear.

The protoxide of lead unites readily with earthy substances, forming with them a transparent colourless glass. Owing to this property, it is much employed for glazing earthen ware and porcelain. It enters in large quantity into the composition of flint glass, which it renders more fusible, transparent, and uniform.

Lead is separated from its salts in the metallic state by iron or zinc. The best way of demonstrating this fact is by dissolving one part of the acetate of lead in sixteen of water, and suspending a piece of zinc in the solution by means of a thread. The lead is deposited upon the zinc in a peculiar arborescent form, giving rise to the appearance

* Annals of Philosophy, vol. xv.

called *arbor Saturni*. This is a convenient method of obtaining very pure metallic lead.

*Deutoxide.*—The deutoxide of lead is the *minium* or *red lead* of commerce, which is employed as a pigment, and in the manufacture of flint glass. It is formed by heating litharge in open vessels, while a current of air is made to play upon its surface.

This oxide does not unite with acids. When heated to redness, it gives off pure oxygen gas, and is reconverted into the protoxide. When digested in nitric acid, it is resolved into the protoxide and peroxide of lead, the former of which unites with the acid, while the latter remains as an insoluble powder.

*Peroxide.*—This oxide may be obtained by the action of nitric acid on minium, as just mentioned; but the most convenient method of preparing it, is by transmitting a current of chlorine gas through a solution of the acetate of lead. In this process, water is decomposed; its hydrogen uniting with chlorine, and its oxygen with the protoxide of lead, gives rise to muriatic acid and the peroxide of lead.

The peroxide of lead is of a pure colour, and does not unite with acids. It is resolved by a red heat into the protoxide and oxygen gas.

*Chloride of Lead.*—This compound, sometimes called *horn lead* or *plumbum corneum*, is slowly formed by the action of chlorine gas on thin plates of lead, and may be obtained more easily by adding muriatic acid or a solution of sea-salt to the acetate or nitrate of lead dissolved in water. This chloride dissolves to a considerable extent in hot water, especially when acidulated with muriatic acid. In solution it is most probably a muriate of the protoxide of lead; but in cooling, the chloride separates in the form of small acicular crystals of a white colour. It fuses at a temperature below redness, and forms, as it cools, a semi-transparent horny mass. It bears a full red heat in close vessels without subliming. According to the analysis of Dr Davy, it is composed of one equivalent of lead and one equivalent of chlorine.

The pigment called *mineral* or *patent yellow* is a compound of the chloride and protoxide of lead. It is prepared for the purposes of the arts by the action of moistened sea-salt on litharge, by which means a portion of the protoxide is converted into chloride of lead, and then fusing the mixture. Soda is set free during this process, and is converted into a carbonate by absorbing carbonic acid from the atmosphere.

*Iodide of lead* is easily formed by mixing a solution of hydriodic acid or hydriodate of potassa with the acetate or nitrate of lead dissolved in water. It is of a rich yellow colour. It is dissolved by boiling water, forming a colourless solution, and is deposited on cooling in yellow crystalline scales of a brilliant lustre. It is composed of one equivalent of iodine and one equivalent of lead.

*Sulphuret of lead* may be made artificially, either by heating together lead and sulphur, or by the action of sulphuretted hydrogen on a salt of lead. It is an abundant natural product, well known by the name of galena. It consists of one equivalent of lead and one equivalent of sulphur.

# CLASS II.

## ORDER III.

## METALS, THE OXIDES OF WHICH ARE REDUCED TO THE METALLIC STATE BY A RED HEAT.

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## SECTION XXII.

### *MERCURY OR QUICKSILVER.*

Mercury is found in the native state, but it occurs more commonly in combination with sulphur as cinnabar. From this ore, the mercury of commerce may be extracted by heating it with lime or iron filings, by which means the mercury is volatilized and the sulphur retained. As prepared on a large scale, it is usually mixed in small quantity with other metals, from which it may be purified by cautious distillation.

Mercury is distinguished from all other metals by being fluid at common temperatures. It has a tin-white colour and strong metallic lustre. It becomes solid at a temperature which is 39 or 40 degrees below zero; and in congealing, evinces a strong tendency to crystallize in octahedrons. It contracts greatly at the moment of congelation; for while its density at 47° F. is 13.545, the specific gravity of frozen mercury is 15.612. When solid it is malleable, and may be cut with a knife. At 680°* F. or near that degree, it enters into ebullition, and condenses again on cool surfaces into metallic globules.

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* At page 37, Dr Turner has quoted a table from the memoir of MM. Dulong and Pettit, giving the boiling point of mercury at 680° F, and the same number is repeated in this place. If I understand the subject correctly, this number of Dulong and Pettit is the *apparent* boiling point of mercury, measured by that metal in glass, *both* heated to the boiling point of the former. When, however, its boiling point is determined by an air thermometer, which is generally admitted to furnish true indications, the French experimenters make it 662°. According to Mr Crighton, the boiling point of mercury, as ascertained by a good mercurial thermometer, making no corrections for the expansion of the glass, or the increasing rate of expansion of the mercury itself, is 656°. This number does not differ much from the corrected number of Dulong and Pettit; and the near coincidence seems to show that there is a pretty accurate compensation between the causes which influence the correctness of the mercurial thermometer, whereby the general indications of the instrument do not vary much from the truth. B.

Mercury, if quite pure, is not tarnished in the cold by exposure to air and moisture; but if it contain other metals, the amalgam of those metals oxidizes readily, and collects as a film upon its surface. Mercury is said to be oxidized by long agitation in a bottle half full of air, and the oxide so formed was called by Boerhaave *ethiops per se;* but it is very probable that the oxidation of mercury observed under these circumstances was solely owing to the presence of other metals. When mercury is exposed to air or oxygen gas, while in the form of vapour, it slowly absorbs oxygen, and is converted into the peroxide of mercury.

The only acids that act on mercury are the sulphuric and nitric acids. The former has no action whatever in the cold; but on the application of heat, the mercury is oxidized at the expense of the acid, pure sulphurous acid gas is disengaged, and a sulphate of mercury is generated. Nitric acid acts energetically upon mercury both with and without the aid of heat, oxidizing and dissolving it with evolution of the deutoxide of nitrogen.

## *Oxides of Mercury.*

Mercury is susceptible of two stages of oxidation, and both its oxides are capable of forming salts with acids. It appears from the researches of Donovan* and Sefstrom†, whose results are confirmed by the experiments of Dr Thomson, that these oxides are formed in the following proportions:—

| | *Mercury.* | *Oxygen.* |
|---|---|---|
| Protoxide . | 200 or one equivalent . | 8 = 208 |
| Peroxide . | 200 . | 16 = 216 |

*Protoxide.*—The protoxide of mercury, which is a black powder, insoluble in water, is best prepared by the process recommended by Donovan. This consists in mixing calomel briskly in a mortar with pure potassa in excess, so as to effect its decomposition as rapidly as possible. The protoxide is then to be washed with cold water, and dried spontaneously in a dark place. These precautions are rendered necessary by the tendency of the protoxide to resolve itself into the peroxide and metallic mercury, a change which is easily effected by heat, by the direct solar rays, and even by day-light. It is on this account very difficult to procure the protoxide of mercury in a state of absolute purity.

This oxide is precipitated from its salts, of which the nitrate is the most interesting, as the black protoxide by pure alkalies; as a white carbonate, which soon becomes dark from the loss of carbonic acid, by alkaline carbonates; as calomel by muriatic acid or any soluble muriate; and as the black protosulphuret by sulphuretted hydrogen. Of these tests, the action of muriatic acid is the most characteristic. The oxide is reduced to the metallic state by copper, phosphorous acid, or protomuriate of tin.

*Peroxide.*—This oxide may be formed either by the combined agency of heat and air, as already mentioned, or by dissolving mercury in nitric acid, and exposing the nitrate so formed to a temperature just sufficient for expelling the whole of the nitric acid. It is commonly known by the name of *red precipitate.*

* Annals of Philosophy, vol. xiv. † Ibid. vol. iii. p. 355.

The peroxide of mercury, thus prepared, is commonly in the form of shining crystalline scales of a red colour. It is soluble to a small extent in water, forming a solution which has an acrid metallic taste, and communicates a green colour to the blue infusion of violets. When heated to redness, it is converted into metallic mercury and oxygen. Long exposure to light has a similar effect. (Guibourt.)

Some of the neutral salts of this oxide, such as the nitrate and sulphate, are converted by water, especially at a boiling temperature, into insoluble yellow sub-salts, and into soluble colourless super-salts. The oxide is separated from all acids as a red, or when hydratic as a yellow precipitate, by the pure and carbonated fixed alkalies. Ammonia and its carbonate cause a white precipitate, which is a double salt, consisting of one equivalent of the acid, one equivalent of the peroxide, and one equivalent of ammonia. Sulphuretted hydrogen, phosphorous acid, and protomuriate of tin, reduce the peroxide into the protoxide; and when added in larger quantity, the first throws down a black sulphuret, and the two latter metallic mercury. The oxide is readily reduced by insertion of a rod of copper.

## *Chlorides of Mercury.*

Mercury unites with chlorine in two proportions; and the researches of Sir H. Davy and Mr Chenevix leave no doubt that these compounds are analogous in composition to the oxides of mercury, that is, are composed of

| | *Mercury.* | *Chlorine.* | |
|---|---|---|---|
| Protochloride . | 200 . | 36 | = 236 |
| Bichloride . . | 200 . | 72 | = 272 |

*Bichloride.*—When mercury is heated in chlorine gas, it takes fire, and burns with a pale red flame, forming the well-known medicinal preparation and virulent poison, *corrosive sublimate* or bichloride of mercury. It is prepared for medical purposes by subliming a mixture of the bisulphate of the peroxide of mercury, with the chloride of sodium or sea-salt. The exact quantities required for mutual decomposition are 296 parts or one equivalent of the bisulphate, to 120 parts or two equivalents of the chloride. Thus,

| One equivalent of the bisulphate of mercury consists of | | Two equivalents of the chloride of sodium consist of |
|---|---|---|
| Sulphuric acid . | 80 or two equiv. | 72 or two equiv. of chlorine. |
| Peroxide of mercury | 216 or one equiv. | 48 or two equiv. of sodium. |
| | 296 | 120 |

and the products are,

| One equivalent of the bichloride of mercury consisting of | | Two equivalents of the sulphate of soda consisting of | |
|---|---|---|---|
| Mercury | 200 or one equivalent. | Sulphuric acid | 80 or two equiv. |
| Chlorine | 72 or two equivalents. | Soda . | 64 or two equiv. |
| | 272 | | 144 |

The bichloride of mercury, when obtained by sublimation, is a semi-transparent colourless substance, of a crystalline texture. It has an acrid, burning taste, and leaves a nauseous metallic flavour on the tongue. Its specific gravity is 5.2. It sublimes at a red heat without change. It requires twenty times its weight of cold, and only twice

its weight of boiling water for solution, and is deposited from the latter, as it cools, in the form of prismatic crystals. Strong alcohol and ether dissolve it in the same proportion as boiling water; and it is soluble in half its weight of concentrated muriatic acid at the temperature of 70° Fahr. With the muriates of ammonia, potassa, soda, and several other bases, it enters into combination, forming double salts, which are more soluble than the chloride itself.

The bichloride of mercury is probably converted, at the moment of being dissolved, into a muriate of the peroxide; at least this view may safely be admitted, since alkalies and other reagents act upon it precisely in the same manner as on other per-salts of mercury. Its aqueous solution is gradually decomposed by light, calomel being deposited.

The presence of mercury in a fluid supposed to contain corrosive sublimate may be detected by concentrating and digesting it with an excess of pure potassa. The oxide of mercury, which subsides, is then sublimed in a small glass tube by means of a spirit lamp, and obtained in the form of metallic globules. Dr Christison informs me that this and other processes recommended by medical jurists for the detection of corrosive sublimate in mixed fluids, are not altogether satisfactory. He is at present engaged in an inquiry on the subject, and will soon make known the result of his researches.

A very elegant method of detecting the presence of mercury is to place a drop of the suspected liquid on polished gold, and to touch the moistened surface with a piece of iron wire or the point of a penknife, when the part touched instantly becomes white, owing to the formation of an amalgam of gold. This process was originally suggested by Mr Sylvester, and has since been simplified by Dr Paris. (Medical Jurisprudence, by Paris and Fonblanque.)

Many animal and vegetable solutions convert the bichloride of mercury into calomel, a portion of muriatic acid being set free at the same time. Some substances effect this change slowly; while others, and especially albumen, produce it in an instant. Thus, when a solution of corrosive sublimate is mixed with albumen, a white flocculent precipitate subsides, which M. Orfila has shown to be a compound of calomel and albumen, and which he has proved experimentally to be inert. (Toxicologie, vol. i.) Consequently, a solution of the white of eggs is an antidote to poisoning by corrosive sublimate.

*Protochloride.*—The protochloride of mercury, or *calomel*, is always generated when chlorine comes in contact with mercury at common temperatures. It may be made by precipitation, by mixing muriatic acid or any soluble muriate with a solution of the protonitrate of mercury. It is more commonly prepared by sublimation. This is conveniently done by mixing 272 parts or one equivalent of the bichloride with 200 parts or one equivalent of mercury, until the metallic globules entirely disappear, and then subliming. When first prepared it is always mixed with some corrosive sublimate, and therefore should be reduced to powder and well washed before being employed for chemical or medical purposes.

The protochloride of mercury is a rare mineral production, called *horn quicksilver*, which occurs crystallized in quadrangular prisms, terminated by pyramids. When obtained by sublimation it is in semi-transparent crystalline cakes; but as formed by precipitation, it is a white powder. Its density is 7.2. It is distinguished from the bichloride by not being poisonous, by having no taste, and by being exceedingly insoluble in water. Acids have little effect upon it; but pure alkalies decompose it, separating the black protoxide of mercury

and uniting with muriatic acid,—products which necessarily imply the decomposition of water. When calomel is boiled in a solution of the muriate of ammonia, it is converted into corrosive sublimate and metallic mercury. Muriate of soda has a similar effect, though in a less degree.

*Iodides of Mercury.*—The protiodide is formed by mixing a solution of the protonitrate of mercury with the hydriodate of potassa; and the deutiodide, by the action of the same hydriodate on any persalt of mercury. The former is yellow, and is composed of one equivalent of iodine and one equivalent of mercury. The other is of an exceedingly rich red colour, and may be used with advantage in painting. It contains twice as much iodine as the yellow iodide. Both these compounds are insoluble in pure water, but are dissolved by a solution of the hydriodate of potassa.

*Bicyanuret of Mercury.*—This compound is best prepared by boiling, in any convenient quantity of water, eight parts of finely levigated ferrocyanate of the peroxide of iron, quite pure and well dried on a sand bath, with eleven parts of the peroxide of mercury in powder, until the blue colour of the ferrocyanate entirely disappears. A colourless solution is formed, which, when filtered and concentrated by evaporation, yields crystals of bicyanuret of mercury in the form of quadrangular prisms. In this process, the oxygen of the oxide of mercury unites with the iron and hydrogen of the ferrocyanic acid; while the metallic mercury enters into combination with the cyanogen. The brown insoluble matter is peroxide of iron. Pure ferrocyanate of iron is easily procured by digesting common Prussian blue of commerce with muriatic acid diluted with ten parts of water, so as to remove the subsulphate of iron and alumina and other impurities which it commonly contains, and then edulcorating the insoluble ferrocyanate till the free acid is removed. (Edinburgh Journal of Science, No. x.)

The bicyanuret of mercury, when pure, is colourless and inodorous, has a very disagreeable metallic taste, and is highly poisonous. It does not affect the colour of litmus or turmeric paper. When strongly heated it is converted into cyanogen and metallic mercury. (Page 250.) It is more soluble in hot than in cold water, and dissolves in that liquid without change. The solution has not the characteristic odour of the salts of hydrocyanic acid, nor do alkalies throw down the oxide of mercury. It is composed of 200 parts or one equivalent of mercury, and 52 parts or two equivalents of cyanogen.

*Sulphurets of Mercury.*—The protosulphuret of mercury may be prepared by transmitting a current of sulphuretted hydrogen gas through a dilute solution of the protonitrate of mercury, or through water in which calomel is suspended. It is a black-coloured substance, convertible into the sulphate of mercury by digestion in strong nitric acid. When exposed to heat, it is resolved into the bisulphuret and metallic mercury. It is composed of 200 parts or one equivalent of mercury, and 16 parts or one equivalent of sulphur.

The bisulphuret is formed by fusing sulphur with about six times its weight of mercury, and subliming in close vessels. When procured by this process it has a red colour, and is known by the name of *factitious cinnabar*. Its tint is greatly improved by being reduced to powder, in which state it forms the beautiful pigment *vermilion*. It may be obtained in the moist way by pouring a solution of corrosive sublimate into an excess of hydrosulphuret of ammonia. A black precipitate subsides, which acquires the usual red colour of cinnabar when sublimed. I apprehend the black precipitate formed by the action of

sulphuretted hydrogen on bicyanuret of mercury, is likewise a bisulphuret. Cinnabar, as already mentioned, occurs native.

When equal parts of sulphur and mercury are triturated together until metallic globules cease to be visible, the dark coloured mass called *ethiops mineral* results, which Mr Brande has proved to be a mixture of sulphur and bisulphuret of mercury. (Journal of Science, vol. xviii. p. 294.)

Cinnabar is not attacked by alkalies, or any simple acid; but it is dissolved by the nitro-muriatic acid, with formation of sulphuric acid and the oxide of mercury. M. Guibourt has shown that it is composed of one equivalent of mercury and two equivalents of sulphur*.

## SECTION XXIII.

### *SILVER.*

This metal frequently occurs native in silver mines, both massive and in octahedral or cubic crystals. It is also found in combination with several other metals, such as gold, antimony, copper, and arsenic, and with sulphur.

Pure silver may be obtained for chemical purposes by placing a clean piece of copper in a solution of the nitrate of silver, washing the precipitated metal with pure water, and then digesting it in ammonia, in order to remove any adhering copper. It may also be prepared from the chloride of silver, either by exposing that compound mixed with a pure or carbonated alkali to a strong heat in a black lead crucible, or by transmitting over it a current of hydrogen gas, when heated to redness in a tube of porcelain.

Silver has the clearest white colour of all the metals, and is susceptible of receiving a lustre surpassed only by polished steel. In malleability and ductility, it is inferior only to gold, and its tenacity is considerable. It is very soft when pure, so that it may be cut with a knife. Its density after being hammered is 10.51. At 20° or 22° of Wedgwood's pyrometer it fuses.

Pure silver does not rust by exposure to air and moisture, nor is it oxidized by fusion in open vessels. It appears, indeed, that a film of oxide is formed when melted silver is exposed to a current of air or oxygen gas; but it spontaneously parts with the oxygen as it becomes solid. When silver in the form of leaves or fine wire is intensely heated by means of electricity, galvanism, or the oxy-hydrogen blowpipe, it burns with vivid scintillations of a greenish-white colour.

The only pure acids that act on silver are the sulphuric and nitric acids, by both of which it is oxidized, forming with the first a sulphate, and with the second, a nitrate of silver. It is not attacked by sulphuric acid unless by the aid of heat. Nitric acid is its proper solvent, and forms with it a salt, which, in its fused state, is known by the name of *lunar caustic*.

*Oxide of Silver.*—The oxide of silver is best procured by mixing

* An. de Ch. et de Ph. vol. i. See also some very judicious observations on the paper of M. Guibourt by Mr Brande, in the Journal of Science, xviii. 291.

a solution of pure baryta with nitrate of silver dissolved in water. This oxide is of a brown colour, insoluble in water, and is completely reduced by a red heat. According to Sir H. Davy, it is composed of 110 parts of silver and 8 parts of oxygen; and, therefore, regarding it as the real protoxide, 110 is the atomic weight of silver.

The oxide of silver is separated from its solution in nitric acid, by pure alkalies and alkaline earths, as the brown oxide, which is redissolved by ammonia in excess; by alkaline carbonates as a white carbonate, which is soluble in an excess of the carbonate of ammonia; as a dark brown sulphuret by sulphuretted hydrogen; and as a white curdy chloride of silver, which is turned violet by light, and is very soluble in ammonia, by muriatic acid or any soluble muriate. By the last character, silver may be both distinguished and separated from other metallic bodies.

Silver is precipitated in the metallic state by most other metals. When mercury is employed for this purpose, the silver assumes a beautiful arborescent appearance, called *arbor Dianæ*. A very good proportion for the experiment is twenty grains of lunar caustic to six drachms or an ounce of water. The silver thus deposited always contains mercury.

When the oxide of silver, recently precipitated by baryta or lime-water, and separated from adhering moisture by bibulous paper, is left in contact for ten or twelve hours with a strong solution of ammonia, the greater part of it is dissolved; but a black powder remains which detonates violently from heat or percussion. This substance, which was discovered by Berthollet, (An. de Chimie, vol. i.), appears to be a compound of ammonia and oxide of silver; for the products of its detonation are metallic silver, water, and nitrogen gas. It should be made in very small quantity at a time, and dried spontaneously in the air.

On exposing a solution of the oxide of silver in ammonia to the air, its surface becomes covered with a pellicle, which Mr Faraday considers to be an oxide containing a smaller proportion of oxygen than that just described. This opinion he has made highly probable; but further experiments are requisite before the existence of this oxide can be regarded as certain.

*Chloride of Silver.*—This compound, which sometimes occurs native in silver mines, is always generated when silver is heated in chlorine gas, and may be prepared conveniently by mixing muriatic acid, or any soluble muriate, with a solution of the nitrate of silver. As formed by precipitation it is quite white; but by exposure to the direct solar rays, it becomes violet, and almost black, in the course of a few minutes; and a similar effect is slowly produced by diffused day-light. Muriatic acid is set free during this change, and, according to Berthollet, the dark colour is owing to a separation of the oxide of silver. (Statique Chimique, vol. i. p. 195.)

The chloride of silver, sometimes called *luna cornea* or *horn silver*, is insoluble in water, and is dissolved very sparingly by the strongest acids; but it is soluble in ammonia. Hyposulphurous acid likewise dissolves it. At a temperature of about 500° F. it fuses, and forms a semi-transparent horny mass on cooling. It bears any degree of heat, or even the combined action of pure charcoal and heat, without decomposition; but hydrogen gas decomposes it readily with formation of muriatic acid. According to the experiments of Berzelius and Dr Thomson, it is composed of 110 parts or one equivalent of silver, and 36 parts or one equivalent of chlorine.

*Iodide of Silver.*—This compound is formed when the hydriodate

of potassa is mixed with a solution of the nitrate of silver. It is of a greenish-yellow colour, is insoluble in water and ammonia, and contains one equivalent of each of its elements.

*Cyanuret of Silver* is formed by mixing hydrocyanic acid with nitrate of silver. It is a white curdy substance, similar in appearance to the chloride of silver, insoluble in water and nitric acid, and soluble in a solution of ammonia. It is decomposed by muriatic acid with formation of hydrocyanic acid and chloride of silver. It consists of one equivalent of each of its elements.

*Sulphuret of Silver.*—Silver has a strong affinity for sulphur. This metal tarnishes rapidly when exposed to an atmosphere containing sulphuretted hydrogen gas, owing to the formation of a sulphuret. On transmitting a current of sulphuretted hydrogen gas through a solution of lunar caustic, a dark brown precipitate subsides, which is a sulphuret of silver. The *silver glance* of mineralogists is a similar compound, and the same sulphuret may be prepared by heating thin plates of silver with alternate layers of sulphur.

The sulphuret of silver, according to the experiments of Berzelius, is a compound of 110 parts or one equivalent of silver, and 16 parts or one equivalent of sulphur.

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## SECTION XXIV.

### *GOLD.*

Gold has hitherto been found only in the metallic state, either pure or in combination with other metals. It occurs massive, capillary, in grains, and crystallized in octahedrons and cubes, or their allied forms. It is sometimes found in primary mountains; but more frequently in alluvial depositions, especially among sand in the beds of rivers, having been washed by water out of disintegrated rocks in which it originally existed.

Gold is the only metal which has a yellow colour, a character by which it is distinguished from all other simple metallic bodies. It is capable of receiving a high lustre by polishing, but is inferior in brilliancy to steel, silver, and mercury. In ductility and malleability, it exceeds all other metals; but it is surpassed by several in tenacity. Its density is 19.3. When pure it is exceedingly soft and flexible. It fuses at 32° of Wedgwood's pyrometer.

Gold may be exposed for ages to air and moisture without change, nor is it oxidized by being kept in a state of fusion in open vessels. When intensely ignited by means of electricity or the oxy-hydrogen blowpipe, it burns with a greenish-blue flame, and is dissipated in the form of a purple powder, which is supposed to be an oxide.

Gold is not oxidized or dissolved by any of the pure acids; for it may be boiled even in nitric acid without undergoing any change. Its only solvents are chlorine and nitro-muriatic acid; and it appears from the observations of Sir H. Davy, that chlorine is the agent in both cases, since the nitro-muriatic acid does not dissolve gold, except when it gives rise to the formation of chlorine. (Page 201.) It is to be inferred, therefore, that the chlorine unites directly with the gold. Whether the resulting solution is really a chloride of the metal, or a muriate of its oxide, generated by the decomposition of water, is

uncertain; but from recent observations of M. Pelletier, which will be mentioned immediately, I conceive the former opinion to be the more probable. There is no inconvenience, however, in regarding it as a muriate, because reagents act upon it as if it were such.

The most convenient method of forming a solution of gold is to digest fragments of the metal in a mixture composed of two measures of muriatic and one of nitric acid, until the acid is saturated. The orange-coloured solution is then evaporated to dryness by a regulated heat, in order to expel the free acid without decomposing the residual chloride of gold. On adding water, the chloride is dissolved, forming a neutral solution of a reddish-brown colour.

*Oxides of Gold.*—The chemical history of the oxides of gold is as yet very imperfect. Berzelius is of opinion that there are three oxides. His protoxide is obtained by decomposing the protochloride of gold by a solution of pure potassa, and is of a dark green colour. The deutoxide or purple oxide is the product of the combustion of gold. The composition of these oxides has not yet been satisfactorily determined, and the very existence of the first, though probable, may be questioned. The only well-known oxide is that which is supposed to exist in the solution of gold combined with muriatic acid. It may be prepared by mixing with a concentrated neutral solution of gold a quantity of pure potassa, exactly sufficient for combining with the muriatic acid. A reddish-yellow coloured precipitate, the hydrous peroxide, subsides, which is rendered anhydrous by boiling, and assumes a brownish-black colour*. The best method of forming it, according to M. Pelletier, is by digesting the muriate with pure magnesia, washing the precipitate with water, and removing the excess of magnesia by dilute nitric acid.

The peroxide of gold is yellow in the state of hydrate, and nearly black when pure, is insoluble in water, and completely decomposed by solar light or a red heat. Muriatic acid dissolves it readily, yielding the common solution of gold; but it forms no definite compound with any acid which contains oxygen. It may indeed be dissolved by the nitric and sulphuric acids; but the affinity is so slight that the oxide is precipitated by the addition of water. It combines, on the contrary, with alkaline bases, such as potassa and baryta, apparently forming regular salts, in which it acts the part of a weak acid. These circumstances have induced M. Pelletier to deny that the peroxide is a salifiable base, and to contend that the muriatic solution of gold is in reality a chloride of the metal. On this supposition, he proposes the term *auric acid* for the peroxide of gold, and to its compound with alkalies he gives the denomination of *aurates*.

The peroxide of gold is thrown down of a yellow colour by ammonia, and the precipitate is an aurate of that alkali. It is a highly detonating compound, analogous to the fulminating silver described in the last section.

As chemists are but imperfectly acquainted with the number and composition of the oxides of gold, it is at present impossible to determine the atomic weight of this metal in a satisfactory manner. According to Berzelius†, 100 parts of gold unite with 12.077, according to Oberkampf‡ with 10.01, and according to Pelletier with 10.03 parts of oxygen to constitute the peroxide. M. Javal§ has more recently

* M. Pelletier in the An. de Ch. et de Ph. vol. xv.

† An de Ch. vol. lxxxiii. ‡ Ibid. lxxx.

§ An. de Ch. et de Ph. vol. xvii.

analyzed the oxide of gold, and finds that the proportion stated by Berzelius is very near the truth. If we adopt the numbers given by this chemist, and regard the peroxide as containing three equivalents of oxygen to one of metal, 200 will be the atomic weight of gold, and 224 the equivalent of its oxide. This view is supported by the experiments of Dr Thomson.

*Chlorides of Gold.*—On concentrating the solution of gold to a sufficient extent by evaporation, the perchloride may be obtained in red prismatic crystals, which become brown when brought to perfect dryness. It deliquesces on exposure to the air, and is dissolved readily by water without residue. At a temperature far below that of redness, it is converted, with evolution of two-thirds of its chlorine, into the yellow insoluble protochloride, from which the chlorine is entirely expelled by a red heat. This protochloride is converted, by being boiled in water, into the soluble perchloride and metallic gold.

The composition of the chlorides of gold was investigated by Berzelius and Pelletier; but the results of their analyses are so very discordant, that no satisfactory conclusion can be drawn from them.

The solution of gold is decomposed by substances which have a strong affinity for oxygen. On adding protosulphate of iron dissolved in water, the iron is oxidized to a maximum, and a copious brown precipitate subsides, which is metallic gold in a state of very minute division. This precipitate, when duly washed with dilute muriatic acid, in order to separate adhering iron, is gold in a state of perfect purity. A similar reduction is effected by most of the metals, and by sulphurous and phosphorous acids. When a piece of charcoal is immersed in the solution of gold, and exposed to the direct solar rays, its surface acquires a coating of metallic gold; and ribands may be gilded by moistening them with a dilute solution of gold, and exposing them to a current of hydrogen or phosphuretted hydrogen gas. When a strong aqueous solution of gold is shaken in a phial with an equal volume of pure ether, two fluids result, the lighter of which is an ethereal solution of gold. From this liquid flakes of metal are deposited on standing, especially by exposure to light, and substances moistened with it receive a coating of metallic gold*.

When the protomuriate of tin is added to a dilute aqueous solution of gold, a purple-coloured precipitate, called the *purple of Cassius*, is thrown down, which is the substance employed in painting on porcelain for giving a pink colour. It appears to be a compound of the peroxide of tin and the purple oxide of gold, in which the former is supposed to act as an acid.

*Sulphuret of Gold.*—On transmitting a current of sulphuretted hydrogen gas through a solution of gold, a black precipitate is formed, which is a sulphuret. It is resolved by a red heat into gold and sulphur, and appears from the analysis of Oberkampf to be composed of 200 parts or one equivalent of gold, and 48 parts or three equivalents of sulphur.

The compounds of gold with the other non-metallic bodies have been little examined.

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* With respect to the revival of gold from its solutions, the reader may consult an Essay on Combustion, by Mrs Fulhame, and a paper by Count Rumford in the Philosophical Transactions for 1798.

## SECTION XXV.

### PLATINUM.

This valuable metal occurs only in the metallic state, associated or combined with various other metals, such as copper, iron, lead, gold, silver, palladium, rhodium, osmium, and iridium. It has hitherto been found chiefly in Brazil, Peru, and other parts of South America, in the form of rounded or flattened grains of a metallic lustre and white colour, mixed with sand and other alluvial depositions. Two years ago, however, M. Boussingault discovered it in a syenitic rock in the province of Antioquia in South America, where it occurs in veins associated with gold. Rich mines of gold and platinum have also been recently discovered in the Uralian mountains. (Edinburgh Journal of Science, No. x.)

Pure platinum has a white colour very much like silver, but of inferior lustre. It is the heaviest of known metals, its density being about 21.5. Its malleability is considerable, though far less than that of gold and silver. It may be drawn into wires, the diameter of which does not exceed the 2000th part of an inch. It is a soft metal, and, like iron, admits of being welded at a high temperature. Dr Wollaston has observed that it is a less perfect conductor of caloric than most other metals.

Platinum undergoes no change from the combined agency of air and moisture; and it may be exposed to the strongest heat of a smith's forge without suffering either oxidation or fusion. On heating a small wire of it by means of galvanism or the oxy-hydrogen blow-pipe, it is fused, and afterwards burns with the emission of sparks. The late Mr Smithson Tennant showed that it is oxidized when ignited with nitre, (Philos. Trans. for 1797); and a similar effect is occasioned by pure potassa and lithia.

Platinum is not attacked by any of the pure acids. Its only solvents are chlorine and nitro-muriatic acid, which act upon it with greater difficulty than on gold. The resulting orange-red coloured liquid, from which the excess of acid should be expelled by cautious evaporation, may be regarded as containing either the chloride of platinum, or the muriate of its oxide.

*Oxides of Platinum.*—According to Berzelius, there are two oxides of platinum, the oxygen of which is in the ratio of 1 to 2*. The protoxide is prepared by the action of potassa on the protochloride of platinum. It is of a black colour, is reduced by a red heat, and is composed of 96.5 parts of platinum, and 8 parts of oxygen. Now, Dr Thomson infers from his researches, that 96 is the atomic weight of platinum, from which it is probable that the two oxides of Berzelius are thus constituted:—

| | Platinum. | Oxygen. |
|---|---|---|
| Protoxide | 96 | 8 |
| Peroxide | 96 | 16 |

The peroxide has not hitherto been obtained in a perfectly pure state. Berzelius supposes it to exist in the muriate of platinum com-

* An. de Chim. vol. xxxviii.

bined with muriatic acid; and Dr Thomson states that it is contained in the sulphate of platinum.

Another oxide was described by Mr E. Davy in the Philosophical Transactions for 1820. It is of a gray colour, and is prepared by heating fulminating platinum with nitrous acid. It appears from his analysis to be composed of 96 parts or one equivalent of platinum, and 12 parts or an equivalent and a half of oxygen. Mr Cooper has likewise described an oxide of platinum; but its existence as a definite compound, distinct from those above described, has not, I conceive, been satisfactorily demonstrated.

*Chlorides of Platinum.*—The perchloride is procured by evaporating the muriate of platinum to dryness at a gentle heat. It is deliquescent, and is soluble in water, alcohol, and ether. The ethereal solution is decomposed by the agency of light, metallic platinum being deposited. It is probable from the analysis of the double chloride of potassium and platinum by Dr Thomson and Berzelius, that the perchloride of platinum is composed of 96 parts or one equivalent of metal, to 72 parts or two equivalents of chlorine; but this inference requires confirmation.

When the perchloride is strongly heated, it parts with some of its chlorine, and is converted into a protochloride, which is resolved by a red heat into platinum and chlorine.

Platinum is distinguished from all other substances by the following circumstances. When pure potassa or a salt of potassa is added to a concentrated solution of platinum, a yellow crystalline precipitate subsides, which is very sparingly soluble in water. When heated to full redness, chlorine gas is disengaged, and the residue consists of metallic platinum and the chloride of potassium. According to the analysis of Thomson, it is composed of

| | | |
|---|---|---|
| Bichloride of platinum | . | 168 or one equivalent. |
| Chloride of potassium | . | 76 or one equivalent. |

Ammonia or its salts produce a similar precipitate, which is composed according to Dr Thomson of

| | | |
|---|---|---|
| Bichloride of platinum | . | 168 or one equivalent. |
| Muriate of ammonia | . | 54 or one equivalent. |

When this compound, which is generally called the *muriate of platinum and ammonia*, is heated to redness, chlorine and muriate of ammonia are evolved, and pure platinum remains in the form of a delicate spongy mass, the power of which in kindling an explosive mixture of oxygen and hydrogen gases has already been mentioned. (Page 142.) This salt affords an easy method of procuring platinum in a metallic state, and of separating it from other metals.

Soda forms with muriate of platinum a double salt, which is soluble in water and alcohol, and crystallizes in flattened, oblique, four-sided prisms of an orange-red colour. According to Dr Thomson, it is a compound of one equivalent of the bichloride of platinum, one equivalent of the chloride of sodium, and eight equivalents of water.

*Sulphuret of Platinum.*—When sulphuretted hydrogen gas is transmitted through a solution of muriate of platinum, a black precipitate is thrown down, which Vauquelin regards as a hydrosulphuret of the oxide of platinum. It absorbs oxygen from the air while in a moist state, giving rise to the formation of sulphuric acid. Its composition has not been determined with accuracy.

A black sulphuret of platinum was procured by Mr E. Davy by heating the metal with sulphur, and Vauquelin obtained a similar compound by igniting the yellow muriate of platinum and ammonia

with twice its weight of sulphur. According to the analysis of these chemists, it contains about 16 per cent of sulphur.

The hydrosulphuret of platinum is converted by the action of nitric acid into a sulphate which possesses remarkable properties. On boiling it in strong alcohol, a black powder is precipitated, which consists, according to Mr E. Davy, of 96 per cent of platinum, together with a little oxygen, nitrous acid, and carbon, the last of which is supposed to be accidental. When this powder is placed on bibulous paper moistened with alcohol, a strong action accompanied with a hissing noise ensues, and the powder becomes red-hot, and continues so until the alcohol is consumed. The substance which remains is pure platinum.

Fulminating platinum may be prepared by the action of ammonia in slight excess on a solution of sulphate of platinum. (E. Davy.) It is analogous to the detonating compounds which ammonia forms with the oxides of gold and silver.

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## SECTION XXVI.

### *PALLADIUM. RHODIUM. OSMIUM. IRIDIUM.*

The four metals to be described in this section are all contained in the ore of platinum, and have hitherto been procured in very small quantity. When the ore is digested in nitro-muriatic acid, the platinum, together with palladium, rhodium, iron, copper, and lead, is dissolved; while a black powder is left, consisting of osmium and iridium.

### *Palladium.*

This metal was discovered in 1803 by Dr Wollaston.* On adding bicyanuret of mercury dissolved in water to a neutral solution of the ore of platinum, either before or after the separation of that metal by muriate of ammonia, a yellowish-white flocculent precipitate is gradually deposited, which is cyanuret of palladium. When this compound is heated to redness, the cyanogen is expelled, and pure palladium remains.

Palladium resembles platinum in colour and lustre. It is both malleable and ductile, and considerably harder than platinum. Its specific gravity varies from 11.3 to 11.8. (Wollaston.) In fusibility, it is intermediate between gold and platinum, and is dissipated in sparks when intensely heated by the oxy-hydrogen blowpipe.

Palladium is oxidized and dissolved by nitric acid, and even the sulphuric and muriatic acids act upon it by the aid of heat; but its proper solvent is nitro-muriatic acid. Its oxide forms beautiful red-coloured salts, from which metallic palladium is precipitated by protosulphate of iron, and all the metals described in the foregoing sections, excepting silver, gold, and platinum.

The oxide of palladium is precipitated by pure potassa, as an orange-coloured hydrate, which becomes black when dried, and is decomposed by a red heat. It consists, according to Berzelius, of nearly 56 parts of palladium and 8 parts of oxygen; so that 56 is most

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* Philosophical Transactions for 1804 and 1805.

probably the atomic weight of the metal itself, and 64 the equivalent of its oxide.

## *Rhodium.*

This metal was discovered by Dr Wollaston at the time he was occupied with the discovery of palladium. On immersing a thin plate of clean iron into the solution from which palladium and the greater part of the platinum have been precipitated, the rhodium, together with small quantities of platinum, copper, and lead, is thrown down in the metallic state; and on digesting the precipitate in dilute nitric acid, the two last metals are removed. The rhodium and platinum are then dissolved by means of nitro-muriatic acid, and the solution, after being mixed with some muriate of soda, is evaporated to dryness. Two double salts result, the muriate of platinum and soda, and the muriate of rhodium and soda, the former of which is soluble and the latter insoluble in alcohol, and may, therefore, be separated from one another by that menstruum. The salt of rhodium is then dissolved in water, and the pure rhodium precipitated by insertion of a rod of zinc.

Rhodium, thus procured, is in the form of a black powder, which requires the strongest heat that can be produced in a wind furnace for fusion, and when fused has a white colour and metallic lustre. It is brittle, and its specific gravity is about 11. It is not attacked by any of the acids when in its pure state; but if alloyed with other metals, such as copper or lead, it is oxidized and dissolved by the nitro-muriatic acid, a circumstance which accounts for its presence in the solution of crude platinum. It is oxidized also by being ignited with nitre. Most of its salts are either red or yellow, and the muriate is of a rose-red colour, from which it has received the name of *rhodium**.

The number deduced by Dr Thomson as the atomic weight of rhodium is 44; and its oxides, according to the same chemist, are thus constituted :—

| | *Rhodium.* | *Oxygen.* |
|---|---|---|
| Protoxide . | 44 | 8 |
| Peroxide . | 44 | 16 |

The protoxide is black, and the peroxide, which is the base of the salts of rhodium, is of a yellow colour. Berzelius, whose results do not accord with those of Dr Thomson, has described a brown oxide; but it is as yet undetermined whether it is a distinct oxide or a mixture of the two others.

## *Osmium and Iridium.*

These metals were discovered by the late Mr Tennant in the year 1803†, and the discovery of iridium was made about the same time by M. Descotils in France. The black powder mentioned at the beginning of this section, is a compound of iridium and osmium, an alloy which Dr Wollaston has detected in the form of flat white grains among fragments of crude platinum. From this alloy, which is quite insoluble in nitro-muriatic acid, Mr Tennant prepared iridium and osmium in the following manner. The black powder mixed with soda

* From ῥόδον a rose.

† Philosophical Transactions for 1804.

was heated to redness in a silver crucible, and the residue, after removing the alkali by means of water, was digested in muriatic acid. In this way two solutions, one alkaline and the other acid, were procured, the former of a deep orange colour, containing the oxide of osmium united with soda, and the latter, the muriate of iridium. From the refractory nature of the alloy it is necessary to ignite with successive portions of soda before the whole of any given quantity of the black powder is oxidized.

*Osmium.*—On neutralizing the alkaline liquid just described, and heating it in a retort, the oxide of osmium, which is both volatile and soluble in water, passes over into the recipient, and is there dissolved in the fluid that accompanies it. The aqueous solution is colourless, and emits a pungent peculiar odour, somewhat like that of chlorine, a property which suggested the name of *osmium**. The oxide of osmium has not been procured free from water, nor has its composition been determined. The infusion of gall-nuts is a delicate test of its presence, striking a purple colour which afterwards acquires a deep blue tint.

The oxide of osmium is precipitated in the metallic state by nearly all the metals, excepting gold and platinum. On agitating it with mercury an amalgam is formed, which, when heated in close vessels, yields pure osmium, capable of supporting a white heat without being volatilized or fused. If ignited in open vessels, it is oxidized and then dissipated in vapour. After exposure to heat, it resists the action of all the acids.

*Iridium.*—The solution of the oxide of iridium in muriatic acid, when first prepared, is of a blue colour; but it afterwards becomes of an olive-green hue, and subsequently acquires a deep red tint. This diversity of colour, which gave origin to the name of iridium, is attributed to the metal passing through different stages of oxidation, an opinion which is probable, though by no means established. Chemists, indeed, are as yet ignorant both of the number and composition of the oxides of iridium.

The muriate of iridium, when deprived of its excess of acid by heat, may be procured in crystals of a deep brown colour by evaporation. This salt is characterized by forming with water a red solution, which is rendered colourless by the pure alkalies or alkaline earths, by sulphuretted hydrogen, infusion of gall-nuts, or by ferrocyanate of potassa. It is decomposed by nearly all the metals excepting gold and platinum, the iridium been thrown down in the metallic state. Iridium may likewise be procured from the muriate by exposing that salt to a red heat.

Iridium is the most infusible metal known; but Mr Children, by means of his large galvanic battery, succeeded in fusing it into a globule of a brilliant metallic lustre and white colour. Its specific gravity in this state is 18.68. It is attacked with great difficulty by nitro-muriatic acid; but is oxidized when heated with nitre.

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* From ὀσμη odour.

# SECTION XXVII.

## *ON METALLIC COMBINATIONS.*

Having completed the history of the individual metals, and of the compounds resulting from their union with the simple non-metallic bodies, I shall treat briefly in the present section of the combinations of the metals with one another. These compounds are called *alloys;* and to those alloys of which mercury is a constituent, the term *amalgam* is applied. It is probable that each metal is capable of uniting in one or more proportions with every other metal, and on this supposition the number of alloys would be exceedingly numerous. This department of chemistry, however, owing to its having been cultivated with less zeal than most other branches of the science, is as yet limited, and our knowledge concerning it imperfect. On this account I shall mention those alloys only to which some particular interest is attached.

Metals do not combine with one another in their solid state, owing to the influence of chemical affinity being counteracted by the force of cohesion. It is necessary to liquefy at least one of them, in which case they always unite, provided their mutual attraction is energetic. Thus brass is formed when pieces of copper are put into melted zinc; and gold unites with mercury at common temperatures by mere contact.

Metals appear to unite with one another in every proportion, precisely in the same manner as sulphuric acid and water. Thus there is no limit to the number of alloys of gold and copper. It is certain, however, that metals have a tendency to combine in definite proportion; for several atomic compounds of this kind occur native. The crystallized amalgam of silver, for example, is composed, according to the analysis of Klaproth, of 64 parts of mercury and 36 of silver, numbers which are so nearly in the ratio of 200 to 110, that the amalgam may be inferred to contain one equivalent of each of its elements. It is indeed possible that the variety of proportion is rather apparent than real, arising from the mixture of a few definite compounds with one another, or with uncombined metal; an opinion not only suggested by the mode in which alloys are prepared, but in some measure supported by observation. Thus on adding successive small quantities of silver to mercury, a great variety of fluid amalgams are apparently produced; but, in reality, the chief, if not the sole compound, is a solid amalgam, which is merely diffused throughout the fluid mass, and may be separated by pressing the liquid mercury through a piece of thick leather.

Alloys are analogous to metals in their chief physical properties. They are opake, possess the metallic lustre, and are good conductors of electricity and caloric. They often differ materially in some respects from the elements of which they consist. The colour of an alloy is sometimes different from that of its constituents, of which brass is a remarkable example. The hardness of a metal is in general increased by being alloyed, and for this reason its elasticity and sonorousness are frequently improved. The malleability and ductility of metals, on the contrary, are usually impaired by combination. Alloys formed of two brittle metals are always brittle; and an alloy composed of a

ductile and a brittle metal is generally brittle, especially if the latter predominate. An alloy of two ductile metals is sometimes brittle.

The density of an alloy is sometimes less, sometimes greater, than the mean density of the metals of which it is composed.

The fusibility of metals is greatly increased by being alloyed. Thus pure platinum, which cannot be completely fused in the most intense heat of a wind-furnace, forms a very fusible alloy with arsenic.

The tendency of metals to unite with oxygen is considerably augmented by being alloyed. This effect is particularly conspicuous when dense metals are liquefied by combination with quicksilver, and is manifestly owing to the loss of their cohesive power. Lead and tin, for instance, when united with mercury, are soon oxidized by exposure to the atmosphere; and even gold and silver combine with oxygen, when the amalgams of those metals are agitated with air. The oxidability of one metal in an alloy appears in some instances to be increased in consequence of a galvanic action. Thus Mr Faraday observed, that an alloy of steel with 100th of its weight of platinum was dissolved with effervescence in dilute sulphuric acid, which was so weak that it scarcely acted on common steel;—an effect which he ascribes to the steel in the alloy being rendered positive by the presence of the platinum.

## *Amalgams.*

Quicksilver unites with potassium when agitated in a glass tube with that metal, forming a solid amalgam. When the amalgam is put into water, the potassium is gradually oxidized, hydrogen gas is disengaged, and the mercury resumes its liquid form. A similar compound may be obtained with sodium. These amalgams may also be procured by placing the negative wire in contact with a globule of mercury, during the process of decomposing potassa and soda by galvanism.

A solid amalgam of tin is employed in making looking-glasses; and an amalgam made of one part of lead, one of tin, two of bismuth, and four parts of mercury, is used for silvering the inside of hollow glass globes. This amalgam is solid at common temperatures; but is fused by a slight degree of heat.

The amalgam of zinc and tin, used for promoting the action of the electrical machine, is made by fusing one part of zinc with one of tin, and then agitating the liquid mass with two parts of mercury placed in a wooden box. Mercury evinces little disposition to unite with iron, and, on this account, it is usually preserved in iron bottles.

The amalgam of silver, as already mentioned, is a mineral production. The process of separating silver from its ores by amalgamation, practised on a large scale at Freyberg in Germany, is founded on the affinity of mercury for silver. On exposing the amalgam to heat, the quicksilver is volatilized and pure silver remains.

Gold unites with remarkable facility with mercury, forming a white-coloured compound. An amalgam composed of one part of gold to eight of mercury is employed in gilding brass. The brass, after being rubbed with the nitrate of mercury in order to give it a thin film of quicksilver, is covered with the amalgam of gold, and then exposed to heat for the purpose of expelling the mercury.

## *Alloys of Arsenic.*

Arsenic has a tendency to render the metals, with which it is al-

loyed, both brittle and fusible. It has the property of destroying the colour of gold and copper. An alloy of copper, with a tenth part of arsenic, is so very similar in appearance to silver, that it has been substituted for it. The whiteness of this alloy affords a rough mode of testing for arsenic; for if arsenious acid and charcoal be heated between two plates of copper, a white stain afterwards appears upon its surface, owing to the formation of an arseniuret of copper.

The presence of arsenic in iron has a very pernicious effect; for even though in small proportion, it renders the iron brittle, especially when heated.

The alloy of tin and arsenic is employed for forming arseniuretted hydrogen gas by the action of muriatic acid. The tin of commerce sometimes contains a minute quantity of this alloy.

An alloy of platinum with ten parts of arsenic is fusible at a heat a little above redness, and may therefore be cast in moulds. On exposing the alloy to a gradually increasing temperature in open vessels, the arsenic is oxidized and expelled, and the platinum recovers its purity and infusibility.

## *Alloys of Tin, Lead, Antimony, and Bismuth.*

Tin and lead unite readily when fused together. Equal parts of these metals constitute an alloy which is more fusible than either separately, and is the common solder of the glaziers. Its point of fusion is about 360° F.

Tin, alloyed with small quantities of antimony, copper, and bismuth, forms the best kind of pewter. Inferior sorts contain a large proportion of lead.

Tin, lead, and bismuth form an alloy which is fused by a temperature below 212° Fahr. The best proportion, according to M. D'Arcet, is eight parts of bismuth, five of lead, and three of tin.

An alloy of three parts of lead to one of antimony constitutes the substance of which types for printing are made.

## *Alloys of Copper.*

Copper forms with tin several valuable alloys, which are characterized by their sonorousness. Bronze is an alloy of copper with about eight or ten per cent of tin, together with small quantities of other metals which are not essential to the compound. Cannons are cast with an alloy of a similar kind.

The best bell-metal is composed of 80 parts of zinc and 20 of tin: the Indian gong, celebrated for the richness of its tones, contains copper and tin in this proportion. A specimen of English bell-metal was found by Dr Thomson to consist of 80 parts of copper, 10.1 of tin, 5.6 of zinc, and 4.3 of lead. Lead and antimony, though in small quantity, have a remarkable effect in diminishing the elasticity and sonorousness of the compound. The *speculum-metal*, with which mirrors for telescopes are made, consists of about two parts of copper and one of tin. The whiteness of the alloy is improved by the addition of a little arsenic.

Copper and zinc unite in several proportions, forming alloys of great importance in the arts. The best brass consists of four parts of copper to one of zinc; and when the latter is in a greater proportion, compounds are generated which are called *Tombac*, *Duch-gold*, and *Pinchbeck*. The *white copper* of the Chinese is composed, accord-

ing to the analysis of Dr Fyfe, of 40.4 parts of copper, 25.4 of zinc, 31.6 of nickel, and 2.6 of iron.

The art of tinning copper consists in covering that metal with a thin layer of tin, in order to protect its surface from rusting. For this purpose, pieces of tin are placed upon a well polished sheet of copper, which is heated sufficiently for fusing the tin. As soon as the tin liquefies, it is rubbed over the whole sheet of copper, and if the process is skilfully conducted, adheres uniformly to its surface. The oxidation of the tin, a circumstance which would entirely prevent the success of the operation, is avoided by employing fragments of resin or muriate of ammonia, and regulating the temperature with great care. The two metals do not actually combine with one another; but the adhesion is certainly owing to their mutual affinity. Iron, which has a weaker attraction than copper for tin, is tinned with more difficulty than that metal.

## *Alloys of Steel.*

Messrs Stodart and Faraday have succeeded in making some very important alloys of steel with other metals. (Philos. Trans. for 1822.) Their experiments induced them to believe that the celebrated Indian steel, called *wootz,* is an alloy of steel with small quantities of silicium and aluminium; and they succeeded in preparing a similar compound, possessed of all the properties of wootz. They ascertained that silver combines with steel, forming an alloy which, although it contains only 1-500th of its weight of silver, is superior to wootz or the best cast steel in hardness. The alloy of steel with 100th part of platinum, though less hard than that with silver, possesses a greater degree of toughness, and is therefore highly valuable when tenacity as well as hardness is required. The alloy of steel with rhodium even exceeds the two former in hardness. The compound of steel with palladium, and of steel with iridium and osmium, is likewise exceedingly hard; but these alloys cannot be employed extensively, owing to the rarity of the metals of which they are composed.

## *Alloys of Silver.*

Silver is capable of uniting with most other metals, and suffers greatly in malleability and ductility by their presence. It may contain a large quantity of copper without losing its white colour. The standard silver for coinage contains about 1-13th part of copper, which increases its hardness, and thus renders it more fit for coins and many other purposes.

## *Alloys of Gold.*

The presence of other metals in gold has a remarkable effect in impairing its malleability and ductility. The metals which possess this property in the greatest degree are bismuth, lead, antimony, and arsenic. Thus, when gold is alloyed with 1-1920th part of its weight of lead, its malleability is surprisingly diminished. A very small proportion of copper has an influence over the colour of gold, communicating to it a red tint, which becomes deeper as the quantity of copper increases. Pure gold, being too soft for coinage and many purposes in the arts, is always alloyed either with copper or an alloy of copper and silver, which increases the hardness of the gold without materially affecting its colour or tenacity. Gold coins contain about 1-12th of copper.

# SALTS.

## *GENERAL REMARKS ON SALTS.*

In the preceding pages I have been chiefly occupied with the description either of elementary principles, or of compounds immediately resulting from their union. The class of bodies which I am now to describe is of a different nature, being exclusively compounds derived from the combination of other compound bodies.

The term *salt* is often somewhat vaguely employed in chemistry, but according to the usage of most chemists, it denotes a definite compound of an acid, and an alkaline or salifiable base, both of which are in every case composed of at least two simple substances. Sulphate of potassa, for instance, is a salt, the acid of which consists of oxygen and sulphur, and the base of oxygen and potassium. A different view may indeed be formed of the nature of a salt. Thus, to employ the example already adduced, sulphate of potassa contains sulphur, oxygen, and potassium; and it may be thought that these three elements do not exist in the salt as sulphuric acid and potassa, but are combined directly and indiscriminately with one another. But such an opinion is gratuitous and untenable. Sulphate of potassa is said to contain sulphuric acid and potassa, because, in the first place, it is formed by the direct mixture of these two substances; secondly, because the acid and the alkali, after combination, may be separated and again procured in their original state by the agency of galvanism; and, thirdly, because no known affinity is in operation by which the tendency of potassium to constitute potassa with oxygen, or of sulphur to form sulphuric acid with the same element, may be counteracted. It is probable, indeed, that all compounds consisting of three or more elementary principles, are composed of binary compounds united with one another.

In studying the salts, it is important to set out with correct ideas concerning the nature of an acid and of an alkaline base, and I shall, therefore, make a few preliminary remarks concerning the nature and characteristic properties of these two classes of compounds.

An acid is commonly regarded as a substance which has a sour taste, reddens litmus paper, and neutralizes alkalies. But these properties, though very conspicuous in all the powerful acids, are not altogether general, and, therefore, cannot serve the purpose of a definition. Thus insoluble acids, owing to their insolubility, do not taste sour, nor redden litmus paper; and some bodies, such as carbonic acid and sulphuretted hydrogen, the title of which to be placed among the acids cannot be called in question, are unable to destroy the alkaline reaction of potassa. The most correct definition of an acid with which I am acquainted is the following;—an acid is a compound which is capable of uniting in definite proportion with alkaline bases,

and which, when liquid or in a state of solution, has either a sour taste, or reddens litmus paper.

Most of the acids contain oxygen as one of their elements, a circumstance which induced Lavoisier to suppose that oxygen possesses some specific power of causing acidity, and for this reason he regarded it as the *acidifying principle*. The acquisition of new facts, however, has shown the fallacy of his opinion. Acids may and do exist which contain no trace of oxygen, nor does its presence necessarily give rise to acidity. The compounds of oxygen are frequently alkaline instead of acid; and in many instances they are neither acid nor alkaline. No substance, excepting the deutoxide of hydrogen, contains a larger proportional quantity of oxygen than water, and yet this fluid does not possess the slightest degree of acidity. The progress of science, indeed, seems to justify the opinion, that there is no body to which the term acidifying principle is strictly applicable. The acidity of any substance cannot be referred to one of its elements rather than the other; but is a new property peculiar to the compound, and to which each of its constituents contributes.

An alkali is characterized by a peculiar pungent taste, by its alkaline reaction on vegetable colours, and by neutralizing acids. There are many salifiable bases, however, which do not possess these characters. Thus pure magnesia, though it is a strong alkaline base, and forms neutral salts with acids, is insipid, and barely produces an appreciable effect on yellow turmeric paper,—an inaction obviously owing to its insolubility. Some compounds neutralize the properties of acids in an imperfect manner, although they form perfect salts. For these reasons, it is desirable to define precisely what is meant by a salifiable base, and the following definition appears to me to answer the purpose. Every compound may be regarded as an alkaline or salifiable base, which forms definite compounds with acids, and which, when liquid or in a state of solution, has an alkaline reaction. All alkaline bases, with the exception of ammonia and the vegetable alkalies, are metallic oxides.

The nomenclature of the salts was explained on a former occasion. (Page 101.) The insufficiency of the division into *neutral*, *super*, and *sub*-salts will be made apparent by the following remarks. In the first place, some alkaline bases form more than one super-salt, in which case two or more different salts would be included under the same name Secondly, some salts have an acid reaction, and might therefore be denominated super-salts, although they do not contain an excess of acid. Nitrate of lead, for instance, has the property of reddening litmus paper; whereas it consists of one equivalent of the oxide of lead and one equivalent of nitric acid, and, therefore, in composition is precisely analogous to nitrate of potassa, which is a neutral salt. This fact was noticed some years ago by Berzelius, who accounted for the circumstance in the following manner. The colour of litmus is naturally red, and it is only rendered blue by the colouring matter combining with an alkali. If an acid be added to the blue compound, the colouring matter is deprived of its alkali, and thus, being set free, resumes its red tint. Now on bringing litmus paper in contact with a salt, the acid and base of which have a weak attraction for each other, it is possible that the alkali contained in the litmus paper may have a stronger affinity for the acid of the salt than the base has with which it was combined; and in that case, the alkali of the litmus being neutralized, its red colour would necessarily be restored. It is hence apparent that a salt may have an acid reaction without having an excess of acid.

As every acid, with few exceptions, is capable of uniting with every alkaline base, and frequently in two or more proportions, it is manifest that the salts must constitute a very numerous class of bodies. It is necessary, on this account, to facilitate the study of them as much as possible by classification. They may be conveniently arranged by placing together those salts which contain either the same salifiable base or the same acid. It is not very material which principle of arrangement is adopted; but I give the preference to the latter, because, in describing the individual oxides, I have already mentioned the characteristic features of their salts, and have thus anticipated the chief advantage that arises from the former mode of classification. I shall, therefore, divide the salts into groups, placing together those saline combinations which consist of the same acid, united with different salifiable bases. The salts of each group, in consequence of containing the same acid, possess certain characters in common, by which they may all be distinguished; and, indeed, the description of many salts, to which no particular interest is attached, is sufficiently comprehended in that of its group, and may, therefore, be omitted.

Nearly all salts are solid, and most of them assume crystalline forms when their solutions are spontaneously evaporated.

The colour of salts is very variable. Those that are composed of a colourless base and acid are always colourless. There is no necessary connection between the colour of an oxide or an acid and that of its salts. A salt though formed of a coloured oxide or acid, may be colourless; and if it is coloured, the tint may differ from that of both its constituents.

All soluble salts are more or less sapid, while those that are insoluble in water are insipid. Few salts are possessed of odour: the only one which is remarkable for this property is the carbonate of ammonia.

Salts differ remarkably in their affinity for water. Thus some salts, such as the nitrates of lime and magnesia, are *deliquescent*, that is, attract moisture from the air, and become liquid. Others, which have a less powerful attraction for water, undergo no change when the air is dry, but become moist in a humid atmosphere; and others may be exposed without change to an atmosphere loaded with watery vapour.

Salts differ likewise in the degree of solubility in water. Some dissolve in less than their weight of water; while others require several hundred times their weight of this liquid for solution, and others are quite insoluble. This difference depends on two circumstances, namely, on the degree of their affinity for water, and on their cohesion; their solubility being in direct ratio with the first, and in inverse ratio with the second. One salt may have a greater affinity for water than another, and yet be less soluble; an effect which may be produced by the cohesive power of the salt which has the stronger attraction for water, being greater than that of the salt which has a less powerful affinity for that liquid. The method proposed by Gay-Lussac for estimating the relative degrees of affinity of salts for water, (An. de Ch. lxxxii.) is by dissolving equal quantities of salts in equal quantities of water, and applying heat to the solutions. That salt which has the greatest affinity for the menstruum will retain it with most force, and will, therefore, require the highest temperature for boiling.

Salts which are soluble in water crystallize more or less regularly when their solutions are evaporated. If the evaporation is rendered rapid by heat, the salt is usually deposited in a confused crystalline

mass; but if it take place slowly, regular crystals are formed. The best mode of conducting the process, is to dissolve a salt in hot water, and when it has become quite cold, to pour the saturated solution into an evaporating basin, which is to be set aside for several days or weeks without being moved. As the water evaporates, the salt assumes the solid form; and the slower the evaporation, the more regular are the crystals. Some salts which are much more soluble in hot than in cold water, crystallize with considerable regularity when a boiling saturated solution is slowly cooled. The form which salts assume in crystallizing is constant under the same circumstances, and constitutes an excellent character by which they may be distinguished from one another.

Many salts during the act of crystallizing unite chemically with a definite portion of water, which forms an essential part of the crystal, and is termed the *water of crystallization*. The quantity of combined water is very variable in different saline bodies, but is uniform in the same salt. A salt may contain more than half its weight of water, and yet be quite dry. On exposing a salt of this kind to heat, it is dissolved, if soluble, in its own water of crystallization, undergoing what is termed the *watery fusion*. By a strong heat, the whole of the water is expelled; for no salt can retain its water of crystallization when heated to redness. Some salts, such as the sulphate and phosphate of soda, lose a portion of their water, and crumble down into a white powder, by mere exposure to the air, a change which is called *efflorescence*. The tendency of salts to undergo this change depends on the dryness and coldness of the air; for a salt which effloresces rapidly in a moderately dry and warm atmosphere, may often be kept without change in one which is damp and cold.

Salts, in crystallizing, frequently inclose mechanically within their texture particles of water, by the expansion of which, when heated, the salt is burst with a crackling noise into smaller fragments. This phenomenon is known by the name of *decrepitation*. Berzelius has correctly remarked that those crystals decrepitate most powerfully, such as the nitrates of baryta and of lead, which contain no water of crystallization.

The atmospheric pressure is said to have considerable influence on the crystallization of salts. If, for example, a concentrated solution, composed of about three parts of sulphate of soda in crystals to two of water, is made to boil briskly, and the flask which contains it is then tightly corked, while its upper part is full of vapour, the solution will cool down to the temperature of the air without crystallizing, and may in that state be preserved for months without change. Before removal of the cork, the liquid may often be briskly agitated without losing its fluidity; but on re-admitting the air, crystallization commonly commences, and the whole becomes solid in the course of a few seconds. The admission of the air sometimes, indeed, fails in causing the effect; but it may be produced with certainty by agitation or the introduction of a solid body. The theory of this phenomenon is not very apparent. Gay-Lussac has shown that it does not depend on atmospheric pressure, (An. de Ch. vol. lxxxvii.); for he finds that the solution may be cooled in open vessels without becoming solid, provided its surface be covered with a film of oil; and I have frequently succeeded in the same experiment without the use of oil, by causing the air of the flask to communicate with the atmosphere by means of a moderately narrow tube. It appears from some experiments of Mr Graham, published in the Philosophical Transactions of Edinburgh for 1828, that the influence of the air may be ascribed to

its uniting chemically with water; for he has proved that gases which are more freely absorbed than atmospheric air, act more rapidly in producing crystallization. Indeed, the rapidity of crystallization, occasioned by the contact of gaseous matter, seems proportional to the degree of its affinity for water.

The same quantity of water may hold several different salts in solution, provided they do not mutually decompose each other. The solvent power of water with respect to one salt is, indeed, sometimes increased by the presence of another, owing to combination taking place between the two salts.

Most salts produce cold during the act of dissolving in water, especially when they are dissolved rapidly and in large quantity. The greatest reduction of temperature is occasioned by those which contain water of crystallization.

All salts are decomposed by Voltaic electricity, provided they are either moistened or in solution. The acid appears at the positive pole of the battery, and the oxide at its opposite extremity; or if the oxide is of easy reduction, the metal itself goes over to the negative side, and its oxygen accompanies the acid to the positive wire.

The composition of salts is subject to the laws of chemical union; and, indeed, the study of these compounds by Wenzel, Richter, and Berzelius, together with the facts ascertained by Dr Wollaston and Dr Thomson, tended materially to establish the doctrine of definite proportion. All salifiable bases, consisting of one equivalent of a metal and one equivalent of oxygen, are converted into neutral salts, that is, into salts without excess either of acid or base, by uniting with one equivalent of an acid. When a metal forms two salifiable bases with oxygen, the peroxide manifests a tendency to unite with more acid than the protoxide, and Gay-Lussac has demonstrated the existence of the following law :—*that the quantity of acid which the oxides of the same metal require for saturation, is in the same ratio as the quantity of oxygen contained in their oxides.* (Memoirs D'Arcueil, vol. ii.) Thus, while the protosulphate of iron contains one equivalent of each of its elements, the soluble persulphate is composed of one equivalent of the peroxide of iron, and one equivalent and a half of sulphuric acid. In like manner, the peroxides of mercury and copper are disposed to unite with two equivalents of acid, or twice as much as would form a neutral salt with the protoxides of those metals. Hence, when a peroxide unites with one equivalent of an acid, the product is commonly a sub-salt.

The combination of salts with one another gives rise to compounds which were formerly called *triple* salts; but as the term *double* salt, proposed by Berzelius, gives a more correct idea of their nature and constitution, I shall always employ it by preference. These salts may be composed either of one acid and two bases, or of two acids and one base, and most probably of two different acids and two different bases. Nearly all the double salts hitherto examined, consist of the same acid and two different bases.

## On Crystallization.

The particles of liquid and gaseous bodies, during the formation of solids, sometimes cohere together in an indiscriminate manner, and give rise to irregular shapeless masses; but more frequently they attach themselves to each other in a certain order, so as to constitute solids possessed of a regularly limited form. The process by which such a body is produced, is called *crystallization;* the solid itself is

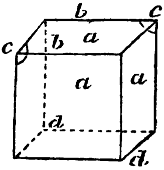
termed a *crystal;* and the science, the object of which is to study the form of crystals, is *crystallography*.

Most bodies crystallize under favourable circumstances. The condition by which the process is peculiarly favoured, is the slow and gradual change of a fluid into a solid, the arrangement of the particles being at the same time undisturbed by motion. This is exemplified during the slow cooling of a fused mass of sulphur or bismuth, or the spontaneous evaporation of a saline solution; and the origin of the numerous crystals, which are found in the mineral kingdom, may be ascribed to the influence of the same cause.

Crystallographers have observed that certain crystalline forms are peculiar to certain substances. Thus calcareous spar crystallizes in rhombohedrons, fluor spar in cubes, and quartz in six-sided pyramids; and these forms are so far peculiar to those substances, that fluor spar is never found in rhombohedrons or six-sided pyramids, nor does calcareous spar or quartz ever occur in cubes. Crystalline form may, therefore, serve as a ground of distinction between different substances. It is accordingly employed by mineralogists for distinguishing one mineral species from another; and it is very serviceable to the chemist as affording a physical character for salts. On this account I have thought it would be useful, before describing the individual salts, to introduce a few pages on crystallization; but from the great extent of the subject, which now constitutes a separate science, my remarks must necessarily be limited, and comprehend little else than an enumeration of the primary forms. To those who are desirous of more ample information, I may recommend Mr Brooke's "Familiar Introduction to Crystallography," or the translation of Mohs's Treatise on Mineralogy by Mr Haidinger.

The surfaces which limit the figure of crystals are called *planes* or *faces*, and are generally flat. The lines formed by the junction of two planes are called *edges;* and the angle formed by two such edges is a *plane angle*. A *solid angle* is the point formed by the meeting of at least three planes. Thus in the cube or hexahedron, figure 1, *a a a* are planes, *b b* are edges, and *c c* solid angles. The cube, it is apparent, has six planes or faces, twelve edges, and eight solid angles. Each of the faces has four angles, which are rectangular.

Fig. 1.




The forms of crystals are exceedingly diversified. They are divided by crystallographers into what are called *primitive, primary, derivative, or fundamental* forms, and into *secondary* or *derived* forms. This distinction is founded on the fact, that the same substance frequently assumes different crystalline forms; which, however, though actually different, are in general geometrically allied to each other. A body, for instance, whose ordinary figure is a cube, may assume a shape represented by figure 2, where the general outline is cubic, but the solid angles are replaced by triangular faces; just as if the crystal had been originally a perfect cube, and its eight solid angles subsequently removed by mechanical means. Instead of the solid angles, the edges of the cube may be wanting, and a new form, such as figure 3, be produced. If the new planes

Fig. 2.

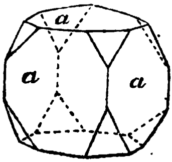
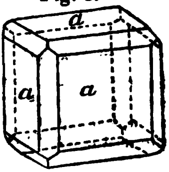


Fig. 3.

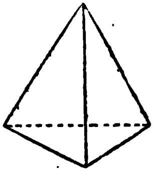



are small, the crystal will preserve its cubic appearance; but if they are larger, the outline of the cube will be less distinct; and should the faces of the original cube wholly disappear, a form altogether different will result. Secondary crystals are those which may be thus deduced by the substitution of planes for the edges or angles of some primary form; and the primary or fundamental form is that from which the former are derived. The replacement is commonly produced by what are called *tangent planes*. By a tangent plane, in reference to the edge of a crystal, is meant a plane inclined equally to the two adjacent primary planes, and parallel to the edge which it replaces. In allusion to a solid angle, a tangent plane is equally inclined on all the primary planes of which the solid angle is constituted.

The number and kind of primary forms are stated differently by different crystallographers, according to the system which they adopt; but I apprehend it will be most advantageous to the chemical student to be acquainted with those enumerated by Mr Brooke in the work above mentioned. They are fifteen number.

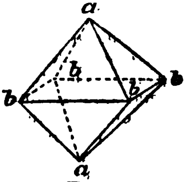
1. The first is the hexahedron or cube of geometricians, a figure bounded by six square faces. All the angles of its edges are also equal to 90 degrees. (Fig. 1.)

Fig. 4.



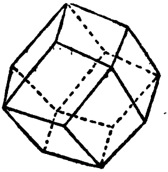
2. The tetrahedron, a regular solid of geometry is contained under four equilateral triangles, and therefore all its plain angles are equal to 60 degrees. The faces incline to each other at the edges at an angle of 70° 31′ 44″. (Fig. 4.)

Fig. 5.



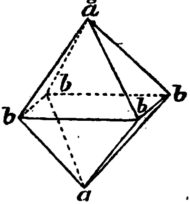

3. The regular octahedron is contained under eight equilateral triangles, figure 5, and consequently all its plane angles are equal to 60 degrees. The base of the octahedron *bbbb* is a square, and the planes incline on each other at the edges at an angle of 109° 28′ 16″. The octahedron is a regular solid of geometry.

Fig. 6.



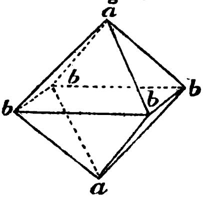
4. The rhombic dodecahedron, figure 6, is limited by twelve similar rhombic faces, the plane angles of which are equal to 109° 28′ 16″ and 70° 31′ 44″. The faces incline to each other at the edges at an angle of 120°.

Fig. 7.



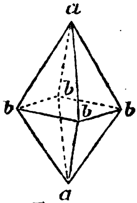

5. The octahedron with a square base, figure 7, is bounded by eight faces which are similar isosceles triangles. The base *bbbb* is always a square, and this is the only part of the figure which is constant.

Fig. 8.



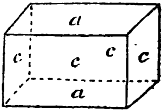

6. The rectangular octahedron, figure 8, is limited by eight isosceles triangles, four of which are different from the other four. The base *bbbb* is always a rectangle; but the ratio of its two sides, as well as all the other dimensions of the figure, is variable.

Fig. 9.



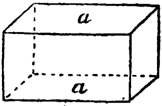

7. The rhombic octahedron, figure 9, is contained under eight faces which are similar scalene triangles, and the base *bbbb* is a rhomb. All its dimensions are variable.

Fig. 10.



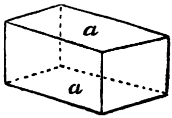

8. The right square prism, figure 10, is a six sided figure, which differs from the cube only in its four *lateral* planes *cccc* being rectangles. The extremities or *terminal* planes *aa* are square. The term *right* denotes that the lateral and terminal planes are inclined to each other at a right angle. It is used in opposition to *oblique*, which signifies that the sides are not perpendicular, but form an oblique angle with the terminal planes.

Fig. 11.



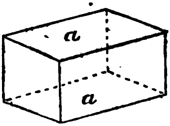

9. The right rectangular prism, figure 11, differs from the former in the terminal planes *aa* being rectangular instead of square.

Fig. 12.



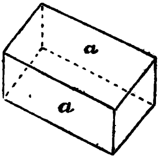

10. The right rhombic prism, figure 12, differs from the two preceding forms only in its terminal planes *aa* being rhombs.

Fig. 13.



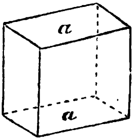

11. The right rhomboidal prism, figure 13, differs from the preceding form in the terminal planes *aa* being rhomboids.

Fig. 14.



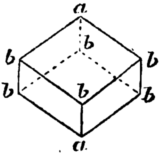

12. In the oblique rhombic prism, the terminal planes *aa* are rhombic, and the lateral planes form an oblique angle with them. (Fig. 14.)

Fig. 15.



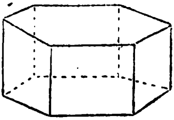

13. The oblique rhomboidal prism, sometimes called the doubly oblique prism, figure 15, differs from the preceding form in the terminal planes *aa* being rhomboids.

Fig. 16.



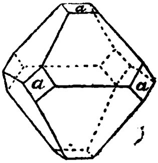

14. The rhombohedron, figure 16, is bounded by six rhombic faces, which are exactly of the same size and form.

Fig. 17.



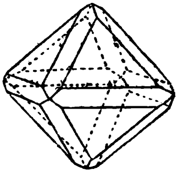
15. The regular hexagonal prism, figure 17, is bounded by six perpendicular or lateral, and two horizontal or terminal planes, which are at right angles to the former. Like the regular hexagon of geometry, the lateral planes incline to each other at an angle of 120 degrees. If these angles are not of 120 degrees, the prism is irregular.

Fig. 18.




The four first forms are geometrically allied to each other. Thus if the six solid angles of the regular octahedron are replaced by tangent planes, as in figure 18, and these are enlarged until they intersect each other, and the faces of the octahedron disappear, a perfect cube is produced. If the twelve edges of the octahedron are replaced by tangent

Fig. 19.



planes, as in figure 19, and these are extended till they mutually intersect, the rhombic dodecahedron will be formed. The cube may by analogous changes be converted into the octahedron, tetrahedron, and rhombic dodecahedron. For if the eight solid angles of the cube be replaced by equilateral triangles, (fig. 2.) and these are enlarged till the planes of the original cube are destroyed, the octahedron results. The tetrahedron may be formed by replacing the four solid angles *cc* and *dd* of the cube (fig. 1.) by tangent planes, so that all its original faces disappear. By replacing the twelve edges of the cube with tangent planes, as in figure 8, until the new faces intersect each other, the rhombic dodecahedron will be produced. By the combination of the planes of different primary forms, various secondary ones are created, as is made obvious by the figures, and will be rendered still clearer by making the transitions above described with an apple or potato. The study of such allied forms is very important, because the same substance often occurs in several of these figures, and may assume all of them.

The octahedron with a square base is allied to the right square prism. Thus if in figure 7, two tangent planes are substituted for the solid angles *aa*, and the edges of the base are replaced by faces perpendicular to the former, new forms will result. If the faces of the octahedron disappear, the right square prism is formed; but if traces of them remain, secondary forms intermediate between the two primary ones will be produced.

The rectangular and rhombic octahedrons, and the right rectangular and rhombic prisms are associated with each other. Thus on replacing the solid angles *aa*, and the four edges of the base of the rectangular octahedron, by tangent planes, and extending them till the planes of the octahedron disappear, the right rectangular prism is formed; and the rhombic octahedron by a similar change is converted into the right rhombic prism. By applying tangent planes to all the edges of the rhombic octahedron except those of the base, the rectangular octahedron may be produced; and by a reversed operation the latter is converted into the former. In this case the solid angles of the rhombic octahedron must be so placed as to bisect the edges of the base of the rectangular octahedron.

The rhombohedron and six sided or hexagonal prism are allied to each other. If tangent planes are laid on the two solid angles *aa* of the rhombohedron, (fig. 16,) and either the six solid lateral angles marked *b*, or the edges between them, are replaced by equal planes perpendicular to the former, a six-sided prism results; and the six-sided prism may be reconverted into the rhombohedron, by replacing all its alternate solid angles by equal and similar rhombic planes.

The six-sided prism is often associated in nature with a double six sided pyramid, formed by all its terminal edges being replaced by isosceles triangles. If the faces of the prism disappear, the double six-sided pyramid results.

The crystalline forms which have an intimate geometrical connection with each other, are considered by crystallographers as constituting certain groups, which are termed *Systems of Crystallization.* Thus, of the fifteen primary forms above described, the Tessular System of Mohs comprehends the cube, the tetrahedron, the regular octahedron, and the rhombic dodecahedron, together with several others not enumerated; his Pyramidical System contains the octa-

hedron with a square base, and the right square prism; the Prismatic System contains the rectangular and rhombic octahedron, and the right rectangular and right rhombic prisms; the Hemiprismatic System includes the right rhomboidal and the oblique rhombic prisms; the oblique rhomboidal prism belongs to the Tetrarto-prismatic System; and the Rhombohedral System comprehends the rhombohedron and the regular hexagonal prism. This distinction is so far important, that all the forms which a salt, or any substance in general assumes, must belong to the same system of crystallization.

Besides the distinction arising from external form, minerals are further distinguished by differences in the mechanical connection of their particles, peculiarities which mineralogists designate by the name of *structure*. The structure of a mineral arises from its particles adhering at some parts less tenaciously than at others, and consequently yielding to force in one direction more readily than at another. Structure is sometimes visible by holding a mineral between the eye and the light; but in general it is brought into view by effecting the actual separation of parts by mechanical means.

The structure of minerals may be *regular* or *irregular*. It is regular when the separation takes place in such a manner, that the detached surfaces are smooth and even, like the planes of a crystal; and it is irregular, when the new surface does not possess this character.

A mineral which possesses a regular structure is said to be *cleavable*, or to admit of *cleavage;* the surfaces exposed by splitting or *cleaving* a mineral are termed the *faces of cleavage;* and the direction in which it may be cleaved is called the *direction of cleavage*. Sometimes a mineral is cleavable only in one direction, and is then said to have a *single* cleavage. Others may be cleaved in two, three, four, or more directions, and are said to have a *double, treble, fourfold* cleavage, and so on, according to their number.

Minerals that are cleavable in more than two directions may, by the removal of layers parallel to the planes of their cleavage, be often made to assume regular primary forms, though they may originally have possessed a different figure. Calcareous spar, for example, occurs in rhombohedrons of different kinds, in hexagonal prisms, in six sided pyramids, and in various combinations of these forms; but it has three sets of cleavage, which are so inclined to each other as to constitute a rhombohedron of invariable dimensions, and into that form every crystal of calcareous spar may be reduced. Lead glance possesses a treble cleavage, the planes of which are at right angles to each other; and hence it is always convertible by cleavage into the cube. The cleavages of fluor spar are fourfold, and in a direction parallel to the planes of the regular octahedron, into which form every cube of fluor may be converted.

Cleavage not only affords a useful character for distinguishing minerals, but is frequently employed by mineralogists for detecting the primary forms of crystals. If a mineral occur in two or more of those forms which have been enumerated as primary, that one is usually selected as fundamental, which may be produced by cleavage. Thus fluor spar is met with in cubes, in the form of the regular octahedron, and as the rhombic dodecahedron. Of these the cube is by far the most frequent; and yet the octahedron is usually adopted as the fundamental form, because fluor has four equally distinct cleavages parallel to the planes of that figure. It is, indeed, a practice very common among mineralogists, not only to consider cleavage as the most influential circumstance in fixing the primary form of a crystal, but to adopt as such no figure which is inconsistent with its cleavages.

Since the forms above enumerated as belonging to the tessular system of crystallization, are possessed of fixed invariable dimensions, it is obvious that minerals or other crystallized bodies included in that system must often in their primary forms be identical with each other. In the other systems of crystallization this identity is not necessary, because the dimensions of their forms are variable. Thus octahedrons with a square base may be distinguished by the relative length of their axis, some being flat and others acute. Rhombic octahedrons may be distinguished from each other by the relative length of their axis, and the angles of their base. By Haüy it was regarded as an axiom in crystallography, that minerals not belonging to the tessular system are characterized by their form; that though two minerals may in form be analogous, each for instance being a rhombic prism, the dimensions of those prisms are different. Identity of form in crystals not included in the tessular system was thought to indicate identity of composition. But in the year 1819, a discovery extremely important both to mineralogy and chemistry was made by Professor Mitscherlich of Berlin, relative to the connection between the crystalline form and composition of bodies. It appears from his researches*, that certain substances are capable of being substituted for each other in combination, without influencing the form of the compound. This singular circumstance has been ably traced by Professor Mitscherlich in the salts of phosphoric and arsenic acids. Thus the neutral phosphate and biphosphate of soda have exactly the same form as the arseniate and binarseniate of soda. The phosphate and biphosphate of ammonia correspond in like manner to the arseniate and binarseniate of ammonia. The neutral phosphate and arseniate of potassa could not be obtained in crystals fit for examination; but the biphosphate and binarseniate of that alkali have the same form. Each arseniate has a corresponding phosphate, possessed of the same form, and containing the same number of equivalents of acid, alkali, and water. These series of salts in fact differ in nothing but in one containing arsenic and the other phosphoric acid.

From these and analogous facts, it appears that certain substances, when similarly combined with the same body, are disposed to affect the same crystalline form. This discovery has led to the formation of groups, each comprehending substances which crystallize in the same manner, and which are hence said to be *isomorphous*. The salts of arsenic acid are isomorphous with those of phosphoric acid. The oxide of lead, baryta, and strontia, when combined with the same acid, yield salts which are said by Professor Mitscherlich to be isomorphous. The salts of lime are isomorphous with those of magnesia, protoxides of manganese, iron, cobalt, and nickel, oxide of zinc, and peroxide of copper. The salts of selenic and sulphuric acids, when similarly united with water and the same base, assume the same form; and the salts of the peroxide of iron are isomorphous with those of alumina.

The similarity of the chemical constitution of isomorphous bodies is peculiarly striking. The first singularity of the kind which merits notice, is the tendency of some isomorphous salts to combine with the same quantity of water of crystallization. This is especially remarkable in the salts of arsenic and phosphoric acids. The biphosphate and binarseniate of potassa crystallize with two equivalents of

* Annales de Ch. et de Physique, vol. xiv. 172, xix. 350, and xxiv. 264 and 355.

water. The neutral phosphate and arseniate of soda contain twelve and a half equivalents of water; and in the biphosphate and binarseniate of soda, four equivalents of water are present. The quantity of water contained in the arseniates of ammonia corresponds to that of the phosphates of ammonia. Indeed scarcely any crystallized artificial arseniate is known, to which a corresponding phosphate has not been discovered. If, on the contrary, two isomorphous salts crystallize with different equivalent quantities of water, their forms are found to differ also. The common sulphates of manganese and copper differ in form from the sulphates of iron and zinc; whereas when their crystals contain the same number of equivalents of water, their form is identical. Mitscherlich has remarked that isomorphous salts, which when pure combine with different proportional quantities of water, are disposed in crystallizing together to unite with the same number of equivalents of water, and assume the same form. The mixed sulphates of iron and copper crystallize together with great facility; and the crystals, though containing a considerable quantity of copper, have the same proportional quantity of water and the same form as the pure protosulphate of iron. According to Mitscherlich, the sulphates of zinc and copper, of copper and magnesia, of copper and nickel, of zinc and manganese, and of magnesia and manganese, crystallize together with six equivalents of water of crystallization, (the same number he states as in protosulphate of iron) and have the same form as green vitriol, without containing a trace of iron. In these instances the isomorphous salts do not occur in definite proportions; so that though they crystallize together, they do not appear to be chemically united.

The similarity in the chemical constitution of isomorphous substances may be illustrated in a different way. Thus, in isomorphous salts, the proportional quantities of acid and base are the same. A neutral phosphate does not correspond to a binarseniate, nor a biphosphate to a neutral arseniate. There is in general also an exact similarity in the composition of the constituents of isomorphous substances. Thus all chemists agree that the atomic constitution of arsenic and phosphoric acids is the same; and the fact is still further evinced by the composition of selenic and sulphuric acids. This singular coincidence led Professor Mitscherlich to believe, that the form of crystals depends on their atomic constitution. He at first suspected that identity of crystalline form is determined solely by the number of atoms, and the mode in which they are united, quite independently of their nature. Subsequent observation, however, induced him to abandon this view; and his opinion now appears to be, that certain elements, which are themselves isomorphous, when combined in the same manner with the same substance, communicate the same form. Similarly constituted salts of arsenic and phosphoric acid yield crystals of the same figure, because the acids, it is thought, are themselves isomorphous; and as the atomic constitution of these acids is similar, each containing the same number of atoms of oxygen united with the same number of atoms of the other ingredient, it is inferred that phosphorus is isomorphous with arsenic. In like manner it is believed that selenic acid must be isomorphous with sulphuric acid, and selenium with sulphur; and the same identity of form is ascribed to all those oxides above enumerated, the salts of which are isomorphous. The accuracy of this ingenious view has not yet been put to the test of extensive observation, because the crystalline forms of the substances in question are for the most part unknown. But

our knowledge, so far as it goes, is favourable; for the peroxide of iron and alumina, the salts of which possess the same form, are themselves isomorphous. It may hence be inferred as probable, that isomorphous compounds in general arise from isomorphous elements uniting in the same manner with the same substance.

The discovery of Professor Mitscherlich, while it serves as a caution to mineralogists against too implicit reliance on crystallographic character, is in several respects of deep interest to the chemist. It tends to lay open fields of inquiry which may not otherwise have been thought of, and thus lead to the discovery of new substances. The tendency of isomorphous bodies to crystallize together accounts for the difficulty of purifying mixtures of isomorphous salts by crystallization. The same property sets the chemist on his guard against the occurrence of isomorphous substances in crystallized minerals. The native phosphates, for example, frequently contain arsenic acid, and conversely the native arseniates, phosphoric acid, without the form of the crystals being thereby affected in the slightest degree. It is likely to afford a useful guide in discovering the atomic constitution of compounds. Thus Berzelius considers peroxide of iron to be composed of two atoms of iron and three atoms of oxygen; and as it is isomorphous with alumina, the composition of the latter is by some thought to be analogous. The similarity in the composition of several other isomorphous compounds gives considerable weight to the argument; but our knowledge of this subject is as yet too limited to excite much confidence. It is possible that aluminium and iron may themselves be not isomorphous, but yield isomorphous oxides by uniting with oxygen in different proportions. The phenomena presented by isomorphous bodies afford a powerful argument in favour of the atomic theory. They are intimately connected with the laws of chemical union; and, like these laws, admit of a satisfactory explanation only by supposing the constitution of matter to be atomic.

In one of the essays above referred to, Professor Mitscherlich observed that the biphosphate of soda is capable of yielding two distinct kinds of crystals, which, though different in form, in composition appeared to be identical. The more uncommon of the two forms resembled the binarseniate of soda; but the more usual form is quite dissimilar. He has since discovered, that sulphur is capable of yielding two distinct kinds of crystals; and infers from his observations that a body, whether simple or compound, can assume two different crystalline forms. The cause of this unexpected fact is not yet ascertained.

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## SECTION I.

### *SULPHATES. SULPHITES. HYPOSULPHATES. HYPOSULPHITES.*

### *Sulphates.*

The salts of sulphuric acid in solution may be detected by muriate of baryta. A white precipitate, the sulphate of baryta, invariably subsides, which is insoluble in all the acids and alkalies, a character

by which the presence of sulphuric acid, whether free or combined, may always be recognised. An insoluble sulphate, such as the sulphate of baryta or strontia, may be detected by mixing it, in fine powder, with three times its weight of carbonate of potassa or soda, and exposing the mixture in a platinum crucible for half an hour to a red heat. Double decomposition ensues; and on digesting the residue in water, filtering the solution, neutralizing the free alkali by pure muriatic, nitric, or acetic acid, and adding muriate of baryta, the insoluble sulphate of that base is precipitated.

Several of the sulphates exist in nature, but the only ones which are abundant are the sulphates of lime and baryta. All of them may be formed by the action of sulphuric acid on the metals themselves, on the metallic oxides or their carbonates, or by way of double decomposition.

The solubility of the sulphates is very variable. There are six only which may be regarded as really insoluble; namely, the sulphates of baryta, tin, antimony, bismuth, lead and mercury. The sparingly soluble sulphates are those of strontia, lime, zirconia, yttria, cerium, and silver. All the others are soluble in water.

All the sulphates, those of potassa, soda, lithia, baryta, strontia, and lime excepted, are decomposed by a white heat. One part of the sulphuric acid of the decomposed sulphate escapes unchanged, and another portion is resolved into sulphurous acid and oxygen. Those which are easily decomposed by heat, such as the sulphate of iron, yield the largest quantity of undecomposed sulphuric acid.

When a sulphate, mixed with carbonaceous matter, is ignited, the oxygen both of the acid and of the oxide unites with carbon, carbonic acid is disengaged, and a metallic sulphuret remains. A similar change is produced by hydrogen gas at a red heat, with formation of water, and frequently of some sulphuretted hydrogen. In some instances, the hydrogen entirely deprives the metal of its sulphur.

The composition of the sulphates, so far as they are subject to general laws, has already been described. (Page 131.)

*Sulphate of Potassa.*—This salt is easily prepared artificially by neutralizing carbonate of potassa with sulphuric acid; and it is procured abundantly as a product of the operation for preparing nitric acid. (Page 166.) Its taste is saline and bitter. It crystallizes in six-sided prisms, bounded by pyramids with six sides. The crystals contain no water of crystallization, and suffer no change by exposure to the air. They decrepitate when heated, and enter into fusion at a red heat. They require sixteen times their weight of water at 60° F. and five of boiling water for solution.

The sulphate of potassa is composed of 40 parts or one equivalent of sulphuric acid, to 48 parts or one equivalent of potassa.

The bisulphate of potassa, which contains twice as much acid as the foregoing salt, is easily formed by digesting 88 parts or one equivalent of the neutral sulphate, with water containing about 50 parts of concentrated sulphuric acid, and evaporating the solution. The form of its crystals is a rhombic prism. It has a strong sour taste, and reddens litmus paper. It is much more soluble than the neutral sulphate, requiring for solution only twice its weight of water at 60° and less than an equal weight at 212° F. It is resolved by heat into sulphuric acid and the neutral sulphate.

*Sulphate of Soda.*—The sulphate of soda, commonly called *Glauber's salt*, is occasionally met with on the surface of the earth, and is frequently contained in mineral springs. It may be made by the direct action of sulphuric acid on carbonate of soda; and it is pro-

cured in large quantity as a residue in the processes for forming muriatic acid and chlorine. (Pages 196 and 201.)

Sulphate of soda has a cooling, saline, and bitter taste. It commonly yields four and six-sided prismatic crystals, but its primary form is a rhombic octahedron. Its crystals effloresce rapidly when exposed to the air, and, according to Berzelius, are composed of 72 parts or one equivalent of the neutral sulphate, and 90 parts or ten equivalents of water. The crystals readily undergo the watery fusion when heated. Water at 60° F. dissolves about one-third of its weight of the crystallized salt, at 72° nearly half its weight, twice its weight at 88°, and 3.2 of its weight at 106°. On increasing the heat beyond this point, a portion of the salt is deposited, being less soluble than at 106°. If a solution saturated at 106° is evaporated at a higher temperature, the salt separates in opake prismatic crystals, which are anhydrous.

The *bisulphate* of soda may be formed in the same manner as the analogous salt of potassa.

*Sulphate of Lithia.*—This salt is very soluble in water, fuses by heat more readily than the sulphates of the other alkalies, and crystallizes in prisms, which resemble the sulphate of soda in appearance, but do not effloresce on exposure to the air. Its taste is saline, without being bitter.

*Sulphate of Ammonia.*—This salt is easily prepared by neutralizing carbonate of ammonia with dilute sulphuric acid; and is contained in considerable quantity in the soot from coal. It crystallizes in long flattened six-sided prisms. It dissolves in two parts of water at 60°, and in an equal weight of boiling water. It is sublimed by heat, but is partially decomposed at the same time. The crystals are composed of 40 parts or one equivalent of acid, and 17 parts or one equivalent of ammonia, combined according to Dr Thomson with one, and according to Berzelius with two, equivalents of water.

*Sulphate of Baryta.*—The native sulphate of baryta, commonly called *heavy spar*, occurs abundantly, chiefly massive, but sometimes in anhydrous crystals, the form of which is variable, being sometimes prismatic and sometimes tabular. Its primary form is a right rhombic prism. Its density is about 4.4. It is easily formed artificially by the way of double decomposition. This salt bears an intense heat without fusing or undergoing any other change, and is one of the most insoluble substances with which chemists are acquainted. It is sparingly dissolved by hot and concentrated sulphuric acid, but it is precipitated by the addition of water. According to Dr Thomson, it is composed of 78 parts or one equivalent of baryta, and 40 parts or one equivalent of sulphuric acid.

*Sulphate of Strontia.*—This salt, the *celestine* of mineralogists, is less abundant than heavy spar. It occurs in prismatic crystals of peculiar beauty in Sicily, and its primary form is a right rhombic prism. Its density is 3.858. As obtained by the way of double decomposition, it is a white heavy powder, very similar to sulphate of baryta. It requires about 3840 times its weight of boiling water for solution. According to Dr Thomson, it consists of 52 parts or one equivalent of strontia, and one equivalent of sulphuric acid.

*Sulphate of Lime.*—This salt is easily formed by mixing a solution of muriate of lime with any soluble sulphate. It occurs abundantly as a natural production. The mineral called *anhydrite* is anhydrous sulphate of lime; and all the varieties of *gypsum* are composed of the same salt, united with water. The pure crystallized specimens of gypsum are sometimes called *selenite*; and the white compact

variety is employed in statuary under the name of *alabaster*. The crystals are generally flattened prisms, the primary form of which is a rhombic prism. The anhydrous compound consists of one equivalent of acid, and 28 parts or one equivalent of lime; and pure gypsum, according to Dr Thomson, is composed of 68 parts or one equivalent of sulphate of lime, and 18 parts or two equivalents of water. The hydrous salt is deprived of its water by a low red heat, and in this state forms plaster of Paris. Its property of becoming hard, when made into a thin paste with water, is owing to the anhydrous sulphate combining chemically with that liquid, and thus depriving it of its fluidity.

Sulphate of lime has hardly any taste. It is considerably more soluble than the sulphates of baryta or strontia, requiring for solution about 500 parts of cold, and 450 of boiling water. Owing to this circumstance, and to its existing so abundantly in the earth, it is frequently contained in spring water, to which it communicates the property called hardness. When freshly precipitated, it may be dissolved completely by dilute nitric acid. It is commonly believed to sustain a white heat without decomposition; but Dr Thomson states, that it parts with some of its acid when heated to redness.

*Sulphate of Magnesia.*—This sulphate, generally known by the name of *Epsom* salt, is frequently contained in mineral springs. It may be made directly, by neutralizing dilute sulphuric acid with carbonate of magnesia; but it is procured for the purposes of commerce by the action of dilute sulphuric acid on magnesian limestone, the native carbonate of lime and magnesia.

Sulphate of magnesia has a saline, bitter, and nauseous taste. It crystallizes readily in small quadrangular prisms, which effloresce slightly in a dry air. It is obtained also in larger crystals, which are irregular six-sided prisms, terminated by six-sided summits. Its primary form is a right rhombic prism, the angles of which are 90° 30′ and 89° 30′. (Brooke.) Its crystals are soluble in an equal weight of water at 60°, and in three-fourths of their weight of boiling water. They undergo the watery fusion when heated; and the anhydrous salt is deprived of a portion of its acid at a white heat. The crystals are composed, according to M. Gay-Lussac, of 60 parts or one equivalent of the dry sulphate, and 63 parts or seven equivalents of water.

On mixing solutions of sulphate of magnesia and sulphate of potassa in atomic proportion, and evaporating, a double salt is formed, which consists of one equivalent of each of the salts and six equivalents of water. The crystals are prismatic, but of a complicated nature, and are connected with an oblique rhombic prism. A similar double salt, isomorphous with the preceding, is formed by spontaneous evaporation from the mixed solutions of sulphate of ammonia and sulphate of magnesia. The crystals contain one equivalent of each of the two salts, and eight equivalents of water.

*Sulphate of Alumina.*—The pure sulphate of alumina is a compound of little interest; but with the sulphate of potassa, it forms an interesting double salt, the well-known alum of commerce.

Alum has a sweetish astringent taste. It is soluble in five parts of water at 60° F. and in little more than its own weight of boiling water. The solution reddens litmus paper; but it is doubtful whether this is owing to an excess of acid, or to the weak affinity existing between alumina and sulphuric acid. (Page 376.) It crystallizes readily in octahedrons, or in segments of an octahedron, and the crystals contain almost 50 per cent of water of crystallization. On being exposed to heat, they froth up remarkably, and part with all the

water, forming anhydrous alum, the *alumen ustum* of the pharmacopœia. At a full red heat, the alumina is deprived of its acid.

There is some doubt as to the real composition of alum. According to Dr Thomson, it is composed of

| | | |
|---|---|---|
| Sulphate of alumina, | 174 | three equivalents. |
| Sulphate of potassa, | 88 | one equivalent. |
| Water, | 225 | twenty-five equivalents. |

Mr Phillips, on the contrary, regards it as a compound of two equivalents of sulphate of alumina, one equivalent of bisulphate of potassa, and twenty-two equivalents of water.

Sulphate of alumina forms with sulphate of ammonia, and with sulphate of soda, double salts, which are very analogous to common alum.

*Sulphate of Manganese.*—This salt is best obtained by dissolving pure carbonate of manganese in moderately dilute sulphuric acid, and setting the solution aside to crystallize by spontaneous evaporation. The crystals are transparent, and of a slight rose tint, in taste resemble Glauber's salt, and occur in flat rhombic prisms. It is insoluble in alcohol, but dissolves in twice and a half times its weight of cold water. If gradually heated, it may be long exposed to a moderate red heat, without losing any of its acid. The crystals are composed of 40 parts or one equivalent of sulphuric acid, 36 parts or one equivalent of the protoxide of manganese, and, according to Mitscherlich, of 45 parts or five equivalents of water.

With sulphate of ammonia, this salt yields a double sulphate of ammonia and manganese, consisting of one equivalent combined with eight of water. It is isomorphous with the analogous salts of magnesia and protoxide of iron.

*Sulphate of Iron.*—The sulphate of the protoxide of iron, commonly called *green vitriol,* is formed by the action of dilute sulphuric acid on metallic iron, (page 144), or by exposing the protosulphuret of iron in fragments to the combined agency of air and moisture. This salt has a strong, styptic, inky taste. Though neutral in composition, being composed of one equivalent of each element, it reddens the vegetable blue colours. It is insoluble in alcohol, but soluble in two parts of cold, and in three-fourths of its weight of boiling water. It occurs in right rhombic prisms, which are transparent, and of a pale green colour. It consists of 76 parts, or one equivalent of the dry salt, combined according to Thomson with seven, and according to Mitscherlich with six, equivalents of water. In the anhydrous state, it is of a dirty white colour. It is this salt which is employed in the manufacture of fuming sulphuric acid. (Page 180.)

Protosulphate of iron forms double salts with sulphate of potassa and sulphate of ammonia, the former of which contains six and the latter eight equivalents of water. They are isomorphous with the analogous double sulphates of magnesia.

The protosulphate of iron absorbs oxygen from the air, especially when in solution, by which an insoluble sub-sulphate of the peroxide of iron is generated, consisting, according to Berzelius, of one equivalent of sulphuric acid, and four equivalents of the peroxide of iron.

When a solution of protosulphate of iron is boiled with a little nitric acid, until the liquid acquires a red colour, and is then evaporated to dryness by a moderate heat, a salt remains, the greater part of which is soluble both in alcohol and water, and which attracts moisture from the atmosphere. The analysis of Berzelius has proved it to be a com-

pound or 40 parts or one equivalent of the peroxide of iron, and 60 parts or an equivalent and a half of sulphuric acid. It is, therefore, a sesquisulphate of the peroxide of iron.

By mixing sulphate of potassa with persulphate of iron, and allowing the solution to crystallize by spontaneous evaporation, crystals are obtained similar to common alum in form, colour, taste, and composition. In this double salt, the sulphate of alumina is replaced by persulphate of iron, with which it is isomorphous.

A similar double salt may be made with a mixture of sulphate of ammonia and persulphate of iron.

*Sulphate of Zinc.*—The sulphate of zinc, frequently called *white vitriol*, is the residue of the process for forming hydrogen gas by the action of dilute sulphuric acid on metallic zinc; but is made, for the purposes of commerce, by roasting the native sulphuret of zinc in a reverberatory furnace. It crystallizes by spontaneous evaporation in transparent flattened four sided prisms, and the primary form of the crystals is a right rhombic prism. The crystals dissolve in two parts and a half of cold, and are still more soluble in boiling water. The taste of this salt is strongly styptic. It reddens vegetable blue colours, though in composition it is a strictly neutral salt, consisting of one equivalent of each of its elements. The crystals are composed of 82 parts or one equivalent of the anhydrous sulphate, and 63 parts or seven equivalents of water.

*Sulphate of Nickel.*—This salt, like the salts of nickel in general, is of a green colour, and crystallizes from its solution in pure water in right rhombic prisms exactly similar to the primary form of sulphate of zinc. If an excess of sulphuric acid is present, the crystals are square prisms, which according to Messrs R. Phillips and Cooper contain rather less water and more acid than the preceding; though the difference is not so great as to indicate a different atomic constitution. (Annals of Philosophy, xxii. 439.) Dr Thomson says he analyzed both kinds, and found their composition identical. They consist of one equivalent of the anhydrous salt and seven equivalents of water. It is soluble in about three times its weight of water at 60° F.

This salt crystallizes with great facility when mixed with sulphate of potassa, as a double sulphate of potassa and nickel. The crystals are of an emerald green colour, soluble in nine parts of cold water, and are composed of one equivalent of sulphate of nickel, one equivalent of sulphate of potassa, and six equivalents of water. Its primary form is an oblique rhombic prism; but the general outline of the crystals is sometimes that of a six-sided prism. It is isomorphous with similar double salts of iron and manganese.

*Sulphates of Copper.*—The sulphate of the protoxide of copper has not been obtained in a separate state. The sulphate of the peroxide of copper, the *blue vitriol* employed by surgeons as an escharotic and astringent, may be prepared for chemical purposes by dissolving peroxide of copper in dilute sulphuric acid; but it is procured for sale by roasting the native sulphuret, so as to bring both its elements to a maximum of oxidation. This salt forms regular crystals of a blue colour, reddens litmus paper, and is soluble in about four of cold, and in two parts of boiling water. According to the researches of Proust, Thomson, and Berzelius, it is composed of 80 parts or one equivalent of the peroxide of copper, 80 parts or two equivalents of acid, and 90 parts or ten equivalents of water. It is, therefore, strictly, a bisulphate.

When pure potassa is added to a solution of the bisulphate of copper, in a quantity which is insufficient for separating the whole of the

acid, a pale bluish-green precipitate, the subsulphate, is thrown down, which is composed of one equivalent of acid and one equivalent of the peroxide.

The sulphate of copper and ammonia is generated by dropping pure ammonia into a solution of the bisulphate, until the sub-salt at first thrown down is nearly all dissolved. It forms a dark blue solution, from which, when concentrated, crystals are deposited by the addition of alcohol. It may be formed also by rubbing briskly in a mortar two parts of the crystallized bisulphate of copper with three parts of carbonate of ammonia, until the mixture acquires a uniform deep blue colour. Carbonic acid gas is disengaged with effervescence during the operation, and the mass becomes moist, owing to the water of the blue vitriol being set free.

This compound, which is the *ammoniaret of copper* of the pharmacopœia, contains sulphuric acid, peroxide of copper, and ammonia; but its precise nature has not been determined in a satisfactory manner. It parts gradually with ammonia by exposure to the air.

*Sulphates of Mercury.*—When two parts of mercury are gently heated in three parts of strong sulphuric acid, so as to cause slow effervescence, a sulphate of the protoxide of mercury is generated. But if a strong heat is employed in such a manner as to excite brisk effervescence, and the mixture is brought to dryness, a pure sulphate of the peroxide results*. The former is composed of one equivalent of sulphuric acid and one equivalent of the protoxide; and the latter of two equivalents of acid and one equivalent of the peroxide. (Thomson.) When this bisulphate, which is the salt employed in making corrosive sublimate, is thrown into hot water, decomposition ensues, and a yellow sub-salt, formerly called *turpeth mineral*, subsides. This salt is composed of one equivalent of the acid and one equivalent of the peroxide. The hot water retains some of the sulphate in solution, together with free sulphuric acid.

## *Sulphites.*

The salts of sulphurous acid have not hitherto been minutely examined. The sulphites of potassa, soda, and ammonia, which are made by neutralizing those alkalies with sulphurous acid, are soluble in water; but most of the other sulphites, so far as is known, are of sparing solubility. The sulphites of baryta, strontia, and lime, are very insoluble, and consequently the soluble salts of these earths decompose the alkaline sulphites.

The stronger acids, such as the sulphuric, muriatic, phosphoric, and arsenic acids, decompose all the sulphites with effervescence, owing to the escape of sulphurous acid, which may easily be recognised by its odour. The nitric acid, by yielding oxygen, converts the sulphites into sulphates.

When the sulphites of the fixed alkalies and alkaline earths are strongly heated in close vessels, a sulphate is generated, and a portion of sulphur sublimed. In open vessels at a high temperature, they absorb oxygen, and are converted into sulphates; and a similar change takes place even in the cold, especially when they are in solution. M. Gay-Lussac has remarked, that a neutral sulphite always forms a

* Donovan in the Annals of Philosophy, vol. xiv.

neutral sulphate when its acid is oxidized; a fact from which it may be inferred, that neutral sulphites consist of one equivalent of the acid and one equivalent of the base.

The hyposulphates and hyposulphites are of little importance, and their general character has already been sufficiently described. (Pages 182 and 183.

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## SECTION II.

### *NITRATES. NITRITES. CHLORATES. IODATES.*

### *Nitrates.*

The nitrates are prepared by the action of nitric acid on metals, on the salifiable bases themselves, or on carbonates. As nitric acid forms soluble salts with all alkaline bases, the acid of the nitrates cannot be precipitated by any reagent. They are readily distinguished from other salts, however, by the three following characters:—1st, by deflagrating with red-hot charcoal; 2d, by their power of dissolving gold leaf on the addition of muriatic acid; 3d, by the evolution of dense, white, acid vapours, which are easily recognised to be nitric acid by their odour, when mixed with strong sulphuric acid.

All the nitrates are decomposed without exception by a high temperature. Some of these salts, of which common nitre is an example, are at first converted, with disengagement of oxygen gas, into nitrites; and then by continuing the heat, the nitrous acid is resolved almost entirely into oxygen and nitrogen gases, and pure potassa remains. In others, such as the nitrates of baryta and strontia, the acid is apparently changed at once into oxygen and nitrogen, without forming a nitrite*. The nitrate of lead, as already mentioned, (p. 163), yields oxygen and nitrous acid; and the nitrate of palladium, which is decomposed without the application of a strong heat, emits nearly pure nitric acid.

As the nitrates are easily decomposed by heat alone, they must necessarily suffer decomposition by the united agency of heat and combustible matter. The nitrates on this account are much employed as oxidizing agents, and frequently act with greater efficacy even than nitro-muriatic acid. Thus metallic titanium, which resists the action of these acids, combines with oxygen when heated with nitre. The efficiency of this salt, which is the nitrate usually employed for the purpose, depends not only on the affinity of the combustible for oxygen, but likewise on that of the oxidized body for potassa. The process for oxidizing substances by means of nitre, is called *deflagration*, and is generally performed by mixing the inflammable body with an

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* There is good reason to believe that the residuum of nitre, after long exposure to a red heat, is the peroxide of potassium, and not pure potassa. (See note, page 282.) So also the nitrates of baryta and strontia, exposed to a regulated red heat, yield the peroxides of barium and strontium. (Pages 291 and 293.) B.

equal weight of the nitrate, and projecting the mixture, in small portions at a time, into a red-hot crucible.

All the neutral nitrates of the fixed alkalies and alkaline earths, together with most of the neutral nitrates of the common metals, are composed of one equivalent of nitric acid, and one equivalent of a protoxide. Consequently, the oxygen of the oxide and acid in all such salts must be in the ratio of 1 to 5.

The only nitrates found native are those of potassa, soda, lime, and magnesia.

*Nitrate of Potassa.*—This salt is generated spontaneously in the soil, and crystallizes upon its surface, in several parts of the world, and especially in the East Indies, whence the greater part of the nitre used in Britain is derived. In France and Germany, it is prepared artificially from a mixture of common mould or porous calcareous earth with animal and vegetable remains containing nitrogen. When a heap of these materials, preserved moist and in a shaded situation, is moderately exposed to the air, nitric acid is gradually generated, and unites with the potassa, lime, and magnesia, which are commonly present in the mixture. On dissolving these salts in water, and precipitating the two earths by carbonate of potassa, a solution is formed, which yields crystals of nitre by evaporation. The nitric acid is probably generated under these circumstances by the nitrogen of the organic matters combining during putrefaction with the oxygen of the atmosphere, a change which must be attributed to the affinity of oxygen for nitrogen, aided by that of nitric acid for alkaline bases.

Nitrate of potassa is a colourless salt, which crystallizes readily in six-sided prisms. Its taste is saline, accompanied with an impression of coolness. It requires for solution seven parts of water at 60° F, and its own weight of boiling water. It contains no water of crystallization, but its crystals are never quite free from water lodged mechanically within them. At 616° F, it undergoes the igneous fusion, and like all the nitrates is decomposed by a red heat.

Nitre is chiefly employed in chemistry as an oxidizing agent, and in the formation of nitric acid. Its chief use in the arts is for making gunpowder, which is a mixture of nitre, charcoal, and sulphur. In the East Indies, it is employed for the preparation of cooling mixtures; an ounce of powdered nitre dissolved in five ounces of water, reduces its temperature by fifteen degrees. It possesses powerful antiseptic properties, and is, therefore, much employed in the preservation of meat and animal matters in general.

*Nitrate of Soda.*—This salt is analogous in its chemical properties to the preceding compound. It sometimes crystallizes in oblique rhombic prisms; but it more commonly occurs as an obtuse rhombohedron, which is its primary form. (Mr Brooke.)

*Nitrate of Ammonia.*—Nitrate of ammonia may be formed by neutralizing dilute nitric acid by carbonate of ammonia, and evaporating the solution. This salt may be procured in three different states, which have been described by Sir H. Davy. (Researches concerning the Nitrous Oxide.) If the evaporation is conducted at a temperature not exceeding 100° F., the salt is obtained in prismatic crystals which are composed, according to the experiments of Davy, Berzelius, and Thomson, of 71 parts or one equivalent of the neutral nitrate of ammonia, and 9 parts or one equivalent of water. If the solution is evaporated at 212° F., fibrous crystals are procured; and if the heat be gradually increased to 300° F., it forms a brittle compact mass on cooling. The fibrous and compact varieties still contain water, the

former 8.2 per cent., and the latter 5.7. All these varieties are deliquescent, and very soluble in water.

The change which the nitrate of ammonia undergoes at a temperature varying between 400° and 500° of F. has already been explained. (Page 158.) When heated to 600°, it explodes with violence, being resolved into water, nitrous acid, deutoxide of nitrogen, and nitrogen. The fibrous variety was found by Sir H. Davy to yield the largest quantity of the protoxide of nitrogen. From one pound of this salt he procured nearly three cubic feet of the gas.

*Nitrate of Baryta.*—This salt is sometimes used as a reagent, and for preparing pure baryta. It is easily prepared by digesting the native carbonate, reduced to powder, in nitric acid diluted with eight or ten times its weight of water. The salt crystallizes readily by evaporation in transparent octahedrons. Its crystals contain no water of crystallization, and are very apt to decrepitate by heat, unless previously reduced to powder. They require twelve parts of water at 60° F., and three or four of boiling water for solution. They undergo the igneous fusion in the fire before being decomposed. They are insoluble in alcohol.

*Nitrate of Strontia.*—This salt may be made from strontianite in the same manner as the foregoing compound, to which it is exceedingly analogous. It is anhydrous, crystallizes in the form of the regular octahedron, and undergoes no change in a moderately dry atmosphere. On some occasions this salt contains water of crystallization; and then assumes the form of a prism with ten sides and two summits. The hydrous salt contains 27.8 per cent of water, according to Mr Cooper.

*Nitrates of Lime and Magnesia.*—These salts are very deliquescent, and soluble in alcohol. By this character the nitrate of lime is easily distinguished and separated from the nitrates of baryta and strontia. (Page 295.)

*Nitrate of Copper.*—This salt is prepared by the action of nitric acid on copper. (Page 159.) It crystallizes, though with some difficulty, in prisms, which are of a deep blue colour, and deliquesce on exposure to the air. The crystals are composed of 108 parts or two equivalents of acid, 80 or one equivalent of the peroxide, and 126 or fourteen equivalents of water. (Thomson.) It is, therefore, strictly a binitrate. The green insoluble subsalt, procured by exposing the binitrate to heat, contains, exclusive of water, one equivalent of acid and one equivalent of the peroxide. When heated to redness, it yields pure peroxide of copper.

*Nitrate of Lead.*—This salt is formed by digesting litharge in dilute nitric acid. It crystallizes readily in octahedrons, which are almost always opake. These crystals are anhydrous. This salt has an acid reaction, but is neutral in composition, consisting of 54 parts or one equivalent of acid, and 112 or one equivalent of the protoxide of lead.

A dinitrate of lead, composed of one equivalent of acid to two equivalents of the protoxide, was formed by Berzelius by adding to a solution of the neutral nitrate, a quantity of pure ammonia insufficient for separating the whole of the acid.

*Nitrates of Mercury.*—The protonitrate is conveniently formed by digesting mercury in nitric acid, diluted with three or four parts of water, until the acid is saturated, and then allowing the solution to evaporate spontaneously in an open vessel. The solution always contains at first some nitrate of the peroxide, but if metallic mercury is left in the liquid, a pure protonitrate is gradually deposited. The salt

thus formed has hitherto been regarded as the neutral protonitrate; but according to the analysis of M. C. G. Mitscherlich, (Poggendorff's Annalen, ix. 387) it is a subsalt, in which the protoxide and acid are in the ratio of 208 to 36. This result, however, requires confirmation. The neutral protonitrate is said by M. C. Mitscherlich to be obtained in crystals, by dissolving the former salt in pure water acidulated with nitric acid, and evaporating spontaneously without the contact of metallic mercury or uncombined oxide. The crystals are composed of 208 parts or one equivalent of the protoxide, 54 parts or one equivalent of acid, and two equivalents of water. These salts dissolve completely in water slightly acidulated with nitric acid, but in pure water a small quantity of a yellow subsalt is generated.

When mercury is heated in an excess of strong nitric acid, it is dissolved with brisk effervescence owing to the escape of the deutoxide of nitrogen, and transparent prismatic crystals of the pernitrate are deposited as the solution cools. It is composed, according to Thomson, of one equivalent of the peroxide and one of the acid; and when put into hot water, it is resolved into a soluble salt, the composition of which is unknown, and into a yellow subsalt. The latter was found by M. Grouvelle to consist of one equivalent of acid to two of the peroxide. (An. de Ch. et Phys. xix.)

*Nitrate of Silver.*—Silver is readily oxidized and dissolved by nitric acid diluted with two or three times its weight of water, forming a solution which yields transparent tabular crystals by evaporation. These crystals, which are anhydrous, undergo the igneous fusion when heated, and assume a crystalline texture in cooling. At a red heat it is completely decomposed, and metallic silver remains. When liquefied by heat, and received in small cylindrical moulds, it forms the *lapis infernalis* or *lunar caustic*, employed by surgeons as a cautery. The nitric acid appears to be the agent which destroys the animal texture, and the black stain is owing to the separation of the oxide of silver. It is sometimes employed for giving a black colour to the hair, and is the basis of the indelible ink for marking linen.

Nitrate of silver deliquesces on exposure to the air. It is soluble in its own weight of cold, and in half its weight of hot water. It dissolves also in four times its weight of alcohol. The aqueous solution undergoes little change if preserved in glass vessels; but when paper moistened with it is exposed to light, especially to sunshine, a black stain is produced, owing to the decomposition of the salt and reduction of the oxide to the metallic state. This solution is employed by chemists as a test of the presence of chlorine and muriatic acid.

Nitrate of silver, even after fusion, reddens vegetable colouring matters; but it is neutral in composition, consisting of one equivalent of acid and one of the oxide.

## *Nitrites.*

Little is known with certainty concerning the compounds of nitrous acid with alkaline bases. The nitrite of potassa is probably formed by heating nitre to redness, and removing it from the fire before the decomposition is complete. On adding a strong acid to the product, red fumes of nitrous acid are disengaged, a character which is common to all the nitrites. Two nitrites of lead have been described in the Annales de Chimie, vol. lxxxiii. by M. Chevreul and M. Berzelius. It is possible, however, that these compounds are hyponitrites.

## Chlorates.

The salts of chloric acid are very analogous to the nitrates. As the chlorates of the alkalies, alkaline earths, and most of the common metals, are composed of one equivalent of chloric acid and one equivalent of a protoxide, it follows that the oxygen of the latter to that of the former is in the ratio of 1 to 5. The chlorates are decomposed by a red heat, nearly all of them being converted into metallic chlorides, with evolution of pure oxygen gas. (Page 204.) They deflagrate with inflammable substances with greater violence than nitrates, yielding oxygen with such facility than an explosion is produced by slight causes. Thus a mixture of sulphur with three times its weight of chlorate of potassa explodes when struck between two hard surfaces. With charcoal, and the sulphurets of arsenic and antimony, this salt forms similar explosive mixtures; and with phosphorus it detonates violently by percussion. The mixture employed in the percussion locks for guns consists of sulphur and chlorate of potassa.

All the chlorates hitherto examined are soluble in water, excepting the protochlorate of mercury, which is of sparing solubility. These salts are distinguished by the action of strong muriatic and sulphuric acids, the former of which occasions the disengagement of chlorine and the protoxide of chlorine, and the latter of the peroxide of chlorine.

None of the chlorates are found native. The only ones that require particular description are the chlorates of potassa and baryta.

*Chlorate of Potassa.*—This salt, formerly called *oxymuriate* or *hyperoxymuriate of potassa*, is colourless, and crystallizes in four and six-sided scales of a pearly lustre. Its primary form is stated by Mr Brooke to be an oblique rhombic prism. It is soluble in sixteen times its weight of water at 60° F., and in two and a half of boiling water. It is quite anhydrous, and when exposed to a temperature of 400° or 500° F. undergoes the igneous fusion. On increasing the heat almost to redness, effervescence ensues, and pure oxygen gas is disengaged, phenomena which have been explained in the section on oxygen.

The chlorate of potassa is made by transmitting chlorine gas through a concentrated solution of pure potassa, until the alkali is completely neutralized. The solution, which, after being boiled for a few minutes, contains nothing but the muriate and chlorate of potassa, (page 197,) is gently evaporated till a pellicle forms upon its surface, and is then allowed to cool. The greater part of the chlorate crystallizes, while the muriate remains in solution. The crystals, after being washed with cold water, may be purified by a second crystallization.

*Chlorate of baryta* is of interest, as being the compound employed in the formation of chloric acid. (Page 203.) The readiest mode of preparing this salt is by the process of Mr Wheeler. On digesting for a few minutes a concentrated solution of chlorate of potassa with a slight excess of silicated hydrofluoric acid, the alkali is precipitated in the form of an insoluble double hydrofluate of silica and potassa, while chloric acid remains in solution. The liquid after filtration is neutralized by carbonate of baryta, which likewise throws down the excess of hydrofluoric acid and silica. The silicated hydrofluoric acid employed in the process is made by conducting fluosilicic acid gas into water.

## *Iodates.*

From the close analogy in the composition of chloric and iodic acids, it follows that the general character of the iodates must be similar to that of the chlorates. Thus in all neutral protiodates, the oxygen contained in the oxide and acid is in the ratio of 1 to 5. They form deflagrating mixtures with combustible matters; and on being heated to low redness, oxygen gas is disengaged and a metallic iodide remains. As the affinity of iodine for metals is less energetic than that of chlorine, many of the iodates part with iodine as well as oxygen when heated, especially if a high temperature is employed.

The iodates are easily recognised by the facility with which their acid is decomposed by deoxidizing agents. Thus the sulphurous, phosphorous, muriatic, and hydriodic acids, deprive the iodic acid of its oxygen, and set iodine at liberty. Sulphuretted hydrogen not only decomposes the acid of these salts, but occasions the formation of hydriodic acid by yielding hydrogen to the iodine. Hence an iodate may be converted into a hydriodate by transmitting a current of sulphuretted hydrogen gas through its solution.

None of the iodates have been found native. They are all of very sparing solubility, or actually insoluble in water, excepting the iodates of the alkalies.

*Iodate of Potassa.*—This salt is easily procured by adding iodine to a concentrated hot solution of pure potassa, until the alkali is completely neutralized. The liquid which contains the iodate and hydriodate of potassa, (page 212) is evaporated to dryness by a gentle heat, and the residue, when cold, is treated by strong alcohol. The iodate, which is insoluble in that menstruum, is left, while the hydriodate of potassa is dissolved.

All the insoluble iodates may be procured from this salt by double decomposition. Thus the iodate of baryta may be formed by mixing muriate of baryta with a solution of iodate of potassa.

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# SECTION III.

## *PHOSPHATES. PHOSPHITES. ARSENIATES. ARSENITES.*

## *Phosphates.*

The neutral salts of phosphoric acid with fixed bases sustain a red heat without decomposition, but they are all fusible at a high temperature. The phosphates of the common metals, at least the greater part of them, are converted into phosphurets by the combined agency of heat and charcoal. The alkaline phosphates are only partially decomposed under these circumstances, and the phosphates of lime, baryta, and strontia, undergo no change. The neutral phosphates, excepting those of potassa, soda, and ammonia, are of sparing solubility in pure water; but they are all dissolved without effervescence in an excess of phosphoric or nitric acid, and are precipitated, for the most part unchanged, from the acid solutions by pure ammonia. Of

all the phosphates, those of baryta, lime, and lead, and especially the latter, are the most insoluble.

The presence of a neutral phosphate in solution may be distinguished by the tests already mentioned in the section on phosphorus. (Page 187.) The insoluble phosphates are decomposed when boiled with a strong solution of carbonate of potassa or soda, the acid uniting with the alkali so as to form a soluble phosphate. The earthy phosphates yield to this treatment with some difficulty, and require continued ebullition.

Several phosphates are met with in the native state, such as those of lime, manganese, iron, uranium, copper, and lead.

*Phosphate of Potassa.*—This salt may be prepared by a process analogous to that described for the formation of phosphate of soda. It is deliquescent and has not been procured in regular crystals. It consists of 35.71 parts or one equivalent of phosphoric acid, and 48 parts or one equivalent of potassa.

The biphosphate may be formed by adding phosphoric acid to carbonate of potassa, until the liquid ceases to yield a precipitate with muriate of baryta, and setting aside the solution to crystallize. The primary form of the crystals is an octahedron with a square base; but they commonly occur in square prisms terminated with the planes of the primary form. They are composed of one equivalent of potassa, two of phosphoric acid, and two equivalents of water. (Mitscherlich.)

*Phosphate of Soda.*—Of the alkaline phosphates, that with base of soda is the one generally employed, owing to the facility with which it is obtained in crystals. It is prepared on a large scale in chemical manufactories, by neutralizing the superphosphate of lime, procured by the action of sulphuric acid on burned bones, (page 184,) with carbonate of soda. The carbonate of lime is separated by filtration, and the clear liquid, after being duly concentrated by evaporation, deposites crystals of the phosphate of soda in cooling.* It commonly contains traces of sulphuric acid, from which it may be purified by repeated solution in distilled water, and crystallization. It is customary in this process to employ a slight excess of the alkali, the presence of which facilitates the formation of crystals. On this account the phosphate of soda has commonly an alkaline reaction; but when carefully prepared, Dr Thomson says it is quite neutral.

This salt crystallizes in oblique rhombic prisms, which effloresce on exposure to the air, and require four parts of cold or two of boiling water for solution. According to the analysis of Mitscherlich, it may be inferred to consist of 35.71 parts or one equivalent of acid, 32 parts or one equivalent of soda, and 112.5 parts or twelve and a half equivalents of water. This salt is employed in medicine as a laxative, and in chemistry as a reagent.

A singular change is produced on this salt by a high temperature. On drying the crystals on a sand bath, they are deprived of twelve equivalents of water, and retain half an equivalent, together with al

* Dr Turner has committed a slight chemical inaccuracy here, similar to that which we noticed in the note to page 187. By the addition of the carbonate of soda to the superphosphate of lime, the excess of acid only is neutralized by the soda, and the carbonic acid is evolved with brisk effervescence, instead of combining with the lime, as Dr Turner supposes. The precipitate is, consequently, *phosphate* and not *carbonate* of lime. *See Thenard, Traité de Chimie, Cinquième Edit. tome ii. p.* 134. B.

their usual characters. But on exposure to a red heat, the remaining half equivalent of water is expelled; and the residual salt, without undergoing any other change of weight, is found to have acquired properties altogether new. On being dissolved in water, and the solution set aside to evaporate spontaneously, crystals are obtained, having the general outline of an irregular six-sided prism, and the primary form of which is a rhombic octahedron. These crystals are permanent in the air, much less soluble in water than the common phosphate, and are composed of one equivalent of acid, one of soda, and five of water. The solution gives a white precipitate with nitrate of silver, quite different in colour and appearance from the yellow precipitate occasioned by the common phosphate.

This remarkable fact, which is yet unexplained, was first noticed by Mr Clarke of Glasgow, who has described the new salt in the Edinburgh Journal of Science, No. xiv. p. 298, under the name of pyrophosphate of soda. The crystals were described by Mr Haidinger in the same number.

In the same Journal, Mr Clarke has described a new phosphate of soda, different from the common one in containing seven and a half instead of twelve and a half equivalents of water. It was formed by exposing a solution of the common phosphate to a uniform temperature of about 90° F. The crystals are permanent in the air, and quite different in form from the common phosphate.

The biphosphate of soda is prepared by adding phosphoric acid to carbonate of soda, until the solution ceases to precipitate muriate of baryta. Being very soluble in water, the solution must be concentrated in order that it may crystallize. This salt is capable of yielding two different kinds of crystals without varying its composition. (Page 388.) The more unusual form, isomorphous with the binarseniate of soda, is a right rhombic prism, the smaller lateral edge of which is 78° 30′, terminated by pyramidal planes. The primary form of its ordinary crystals is a right rhombic prism, the smaller angle of which is 93° 54′.

A double phosphate of potassa and soda may be formed by neutralizing biphosphate of potassa with carbonate of soda. The primary form of its crystals is an oblique rhombic prism, which frequently occurs without any modification. The crystals consist of one equivalent of each base, and two of acid.

*Phosphate of Soda and Ammonia.*—This salt is easily prepared by dissolving one equivalent of muriate of ammonia and two equivalents of phosphate of soda in a small quantity of boiling water. As the liquid cools, prismatic crystals of the double phosphate are deposited, while muriate of soda remains in solution. Their primary form is an oblique rhombic prism. This salt has been long known by the name of *microcosmic salt*, and is much employed as a flux in experiments with the blowpipe. When heated it parts with its water and ammonia, and a very fusible biphosphate of soda remains. It is composed of one equivalent of the phosphate of soda, one equivalent of the phosphate of ammonia, and ten equivalents of water. (Mitscherlich.)

*Phosphate of Ammonia.*—This salt is formed by adding ammonia to concentrated phosphoric acid until a precipitate appears. On applying heat, the precipitate is dissolved, and on abandoning the solution to itself, the neutral salt crystallizes. The primary form of the crystals is an oblique rhombic prism, the smaller lateral angle of which is 84° 30′. They often occur in rhombic prisms with dihedral summits. They appear to contain an equivalent and a half of water. (Mitscherlich.)

The biphosphate is made in the same manner as the preceding bi-

phosphates. The crystals are less soluble than the neutral phosphate, and undergo no change on exposure to the air. Their primary form is an octahedron with a square base; but the right square prism, terminated by the faces of the primary form, is the most frequent. They consist of one equivalent of ammonia, two of acid, and three of water.

*Phosphate of Lime.*—Chemists differ exceedingly as to the number of compounds which phosphoric acid is capable of forming with lime. There seems no doubt, however, from the researches of Berzelius and others, that the phosphate of lime, as it exists in bones, or as obtained by mixing muriate of lime with neutral phosphate of soda in excess, is composed of 35.71 parts or one equivalent of phosphoric acid, and 28 or one equivalent of lime. This is the compound of which many urinary concretions consist.

The biphosphate of lime may be prepared by dissolving phosphate of lime in a slight excess of phosphoric acid. It is very soluble in water, but does not crystallize. A superphosphate is also formed by the action of sulphuric acid on phosphate of lime; but whether it is really a biphosphate, or some super-salt with a still larger proportion of acid, is as yet uncertain. The biphosphate exists in the urine.

*Phosphate of Ammonia and Magnesia.*—The simple phosphate of magnesia, which is prepared by mixing a solution of the sulphate of magnesia with phosphate of soda, is of little interest; but the double phosphate is of importance as constituting a distinct species of urinary concretion. It is easily procured by adding carbonate of ammonia and afterwards phosphate of soda to a solution of sulphate of magnesia, when the double phosphate subsides in the form of minute crystalline grains. This salt is insoluble in pure water; but is dissolved by most acids, even by the acetic, and is precipitated unchanged when the solution is neutralized by ammonia.

The composition of this salt has not been satisfactorily determined. On exposure to heat it emits water and ammonia, and a compound of phosphoric acid and magnesia is left, which is insoluble in water, but is dissolved by strong acids. When strongly heated, it undergoes the igneous fusion, and yields a white enamel. According to Stromeyer, the salt, after being exposed to a red heat, contains 37 per cent of magnesia.

*Phosphites* and *Hypophosphites.*—These compounds have hitherto been little examined, and are of no material importance. They do not, therefore, require a particular description. (Page 188.)

## Arseniates.

All the arseniates are sparingly soluble in water, excepting those of potassa, soda, ammonia, and perhaps lithia; but they are all dissolved without effervescence by dilute nitric acid, as well as most other acids which do not precipitate the base of the salt, and are thrown down again unchanged by pure ammonia. Most of them bear a red heat without decomposition; but they are all decomposed by being heated to redness along with charcoal, metallic arsenic being set at liberty. The arseniates of the fixed alkalies and alkaline earths require a rather high temperature for reduction; while the arseniates of the common metals, such as those of lead and copper, are easily reduced in a glass tube by means of a spirit lamp without danger of melting the glass. Of all the arseniates that of lead is the most insoluble.

The soluble arseniates are easily recognised by the tests described in the section on arsenic; (page 329;) and the insoluble arseniates,

when boiled in a strong solution of the fixed alkaline carbonates, are deprived of their acid, which may then be detected in the usual manner. The free alkali, however, should first be exactly neutralized by pure nitric acid.

The arseniates of lime, nickel, cobalt, iron, copper, and lead, are natural productions.

Arsenic acid unites in two proportions with potassa, soda, and ammonia, forming neutral and bi-salts, all of which, the neutral arseniate of potassa excepted, may be obtained in crystals. They are all formed by adding arsenic acid to the alkaline carbonates, in the manner described for forming the phosphates. The binarseniate of potassa may be formed conveniently by heating to redness equal parts of nitrate of potassa and arsenious acid, and continuing the heat until the effervescence arising from the nitre has ceased. These salts are so similar to the corresponding phosphates both in form and composition, that a particular description is unnecessary.

## *Arsenites.*

The only soluble compounds of arsenious acid and salifiable bases known to chemists, are the arsenites of potassa, soda, and ammonia, which may be prepared by boiling a solution of these alkalies in arsenious acid. The other arsenites are insoluble, or, at most, sparingly soluble in pure water; but they are dissolved by an excess of their own acid, with great facility by nitric acid, and by most other acids with which their bases do not form insoluble compounds. The insoluble arsenites are easily formed by the way of double decomposition.

On exposing the arsenites to heat in close vessels, either the arsenious acid is dissipated in vapour, or they are converted, with disengagement of some metallic arsenic, into arseniates. Heated with charcoal or black flux, the acid is reduced with facility. (Page 269.)

The soluble arsenites, if quite neutral, are characterized by forming a yellow arsenite of silver when mixed with the nitrate of that base, and a green arsenite of copper, *Scheele's green*, with sulphate of copper. When acidulated with acetic or muriatic acid, sulphuretted hydrogen causes the formation of orpiment. The insoluble arsenites are all decomposed when boiled in a solution of carbonate of potassa or soda.

The arsenite of potassa is the active principle of Fowler's arsenical solution.

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# SECTION IV.

## *CHROMATES. BORATES. FLUOBORATES.*

## *Chromates.*

The salts of chromic acid are mostly either of a yellow or red colour, the latter tint predominating whenever the acid is in excess. The chromates of the common metals are decomposed by a strong red heat, by which the acid is resolved into the green oxide of chromium and oxygen gas; but the chromates of the fixed alkalies sustain

a very high temperature without decomposition. They are all decomposed without exception by the united agency of heat and combustible matter.

The chromates are in general sufficiently distinguished by their colour. They may be known chemically by the following character:—On boiling a chromate in muriatic acid mixed with alcohol, the chromic acid is at first set free, and is then decomposed, a green muriate of the oxide of chromium being generated.

The only native chromate hitherto discovered is the red chromate of lead from Siberia, in the examination of which Vauquelin made the discovery of chromium.

*Chromates of Potassa.*—The chromate of potassa, from which all the compounds of chromium are directly or indirectly prepared, is made by heating to redness the native oxide of chromium and iron, commonly called *chromate of iron*, with an equal weight of nitrate of potassa, when chromic acid is generated, and unites with the alkali of the nitre. After digesting the ignited mass in water until the chromate is dissolved, the solution is neutralized by nitric acid, and concentrated by evaporation, in order that the nitrate of potassa should crystallize. The residual liquid is then set aside to evaporate spontaneously, and the chromate is gradually deposited in small prismatic crystals of a lemon-yellow colour. The primary form of its crystals, according to Mr Brooke, is a right rhombic prism.

Chromate of potassa has a cool, bitter, and disagreeable taste. It is soluble to great extent in boiling water, and in twice its weight of that liquid at 60° Fahr. It is insoluble in alcohol. It has an alkaline reaction, and on this account M. Tassaert* regards it as a subsalt; but Dr Thomson has proved that it is neutral in composition, consisting of 52 parts or one equivalent of chromic acid, and 48 parts or one equivalent of potassa. Its crystals are anhydrous†.

The bichromate of potassa, which is made in large quantity at Glasgow for dyeing, is prepared by acidulating the neutral chromate with sulphuric acid, and allowing the solution to crystallize by spontaneous evaporation. When slowly formed it is deposited in four-sided tabular crystals, the primary form of which is an oblique rhombic prism. They have an exceedingly rich red colour, are anhydrous, and consist of one equivalent of the alkali, and two equivalents of chromic acid. (Thomson.) They are soluble in about ten times their weight of water at 60° F., and the solution reddens litmus paper.

The insoluble salts of chromic acid, such as the chromates of baryta, lead, protoxide of mercury, and silver, are prepared by mixing the soluble salts of those bases with a solution of the chromate of potassa. The two former are yellow, the third orange-red, and the fourth deep red or purple. The yellow chromate of lead, which consists of one equivalent of acid, and one equivalent of oxide, is now extensively used as a pigment.

A dichromate of lead, composed of one equivalent of chromic acid, and two equivalents of the protoxide of lead, may be formed by boiling carbonate of lead with excess of chromate of potassa. It is of a beautiful red colour, and has been recommended by Mr Badams as a pigment. (Annals of Philosophy, N. S. vol. ix. p. 303.)

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* An. de Ch. et de Ph. vol. xxii.

† Ann. of Phil. vol. xvi.

## *Borates.*

As the boracic is a feeble acid, it neutralizes the alkalies in an imperfect manner, and on this account the borates of soda, potassa, and ammonia have always an alkaline reaction. For the same reason, when the borates are digested in any of the more powerful acids, such as the sulphuric, nitric, or muriatic, the boracic acid is separated from its base. This does not happen, however, at high temperatures; for boracic acid, owing to its fixed nature, decomposes at a red heat all salts, not excepting sulphates, the acid of which is volatile.

The borates of the alkalies are soluble in water, but all the other salts of this acid are of sparing solubility. They are not decomposed by heat, and the alkaline and earthy borates resist the action of heat and combustible matter. They are remarkably fusible in the fire, a property obviously owing to the great fusibility of boracic acid itself.

The borates are distinguished by the following character:—By digesting any borate in a slight excess of strong sulphuric acid, evaporating to dryness, and boiling the residue in strong alcohol, a solution is formed, which has the property of burning with a green flame. (Page 191.)

*Biborate of Soda.*—This salt, the only borate of importance, occurs native in some of the lakes of Thibet and Persia, and is extracted from this source by evaporation. It is imported from India in a crude state, under the name of *Tincal*, which, after being purified, constitutes the *refined borax* of commerce. It is frequently called *subborate of soda*, a name suggested by the inconsistent and unphilosophical practice, now quite inadmissible, of regulating the nomenclature of salts merely by their action on vegetable colouring matter. It crystallizes in hexahedral prisms, which effloresce on exposure to the air, and require twenty parts of cold, and six of boiling water for solution. When exposed to heat, the crystals are first deprived of their water of crystallization, and then fused, forming a vitreous transparent substance, called *glass of borax*. The crystals, according to the analysis of Dr Thomson, are composed of 48 parts or two equivalents of boracic acid, 32 or one equivalent of soda, and 72 or eight equivalents of water.

The chief use of borax is as a flux, and for the preparation of boracic acid. The biborate of magnesia is a rare natural production, which is known to mineralogists by the name of *boracite*.

*Fluoborates.*—The compounds of fluoboric acid with salifiable bases are as yet almost entirely unknown. Dr Davy ascertained that it unites with ammoniacal gas in three proportions, forming salts, one of which is solid, and the two others liquid.

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# SECTION V.

## *CARBONATES.*

The carbonates are distinguished from other salts by being decomposed with effervescence, owing to the escape of carbonic acid gas, by nearly all the acids.

All the carbonates, excepting those of potassa, soda, and lithia, may be deprived of their acid by heat. The carbonates of baryta and

strontia, and especially the former, require an intense white heat for decomposition; those of lime and magnesia are reduced to the caustic state by a full red heat; and the other carbonates part with their carbonic acid when heated to dull redness.

All the carbonates, excepting those of potassa, soda, and ammonia, are of sparing solubility in pure water; but all of them are more or less soluble in an excess of carbonic acid, owing doubtless to the formation of super-salts.

The former nomenclature of the salts is peculiarly exceptionable as applied to the carbonates. The two well known carbonates of potassa, for example, are distinguished by the prepositions *sub* and *super*, as if the one had an alkaline, and the other an acid reaction; whereas, in fact, according to their action on test paper, they are both sub-salts. I shall adopt the nomenclature which has been employed with other salts, applying the generic name of carbonate to those salts which contain one equivalent of carbonic acid, and one equivalent of the base,—compounds which may be regarded as neutral in composition, however they may act on the colouring matter of plants.

Several of the carbonates occur native, among which may be enumerated the carbonates of soda, baryta, strontia, lime, magnesia, manganese, protoxide of iron, copper, lead, and the double carbonate of lime and magnesia.

*Carbonate of Potassa.*—This salt is procured in an impure form by burning land plants, lixiviating their ashes, and evaporating the solution to dryness, a process which is performed on a large scale in Russia and America. The carbonate of potassa, thus obtained, is known in commerce by the names of *potash* and *pearlash*, and is employed in many of the arts, especially in the formation of soap and the manufacture of glass. When derived from this source, it always contains other salts, such as the sulphate and muriate of potassa; and, therefore, for chemical purposes, should be prepared from cream of tartar, the bitartrate of potassa. On heating this salt to redness, the tartaric acid is decomposed, and a pure carbonate of potassa mixed with charcoal remains. The carbonate is then dissolved in water, and, after filtration, is evaporated to dryness in a capsule of platinum or silver.

Pure carbonate of potassa has a taste strongly alkaline, is slightly caustic, and communicates a green to the blue colour of the violet. It dissolves in less than an equal weight of water at 60° F., deliquesces rapidly on exposure to the air, and crystallizes with much difficulty from its solution. In pure alcohol it is insoluble. It fuses at a full red heat, but undergoes no other change. According to the analysis of Dr Wollaston, it is composed of 22 parts or one equivalent of carbonic acid, and 48 parts or one equivalent of potassa.

The purity of any given specimen of this salt is conveniently ascertained by means of sulphuric acid of specific gravity 1.141. Of this acid, 355 grains neutralize 100 grains of pure carbonate of potassa. (Dr Henry.)

*Bicarbonate of Potassa* is made by transmitting a current of carbonic acid gas through a solution of the carbonate of potassa. By slow evaporation, the bicarbonate is deposited from the liquid in prisms with eight sides, terminated with dihedral summits. Its primary form is a right rhomboidal prism.

The bicarbonate of potassa, though far milder than the carbonate, is alkaline both to the taste and to test paper. It does not deliquesce on exposure to the air. It requires four times its weight of water at 60° F. for solution, and is much more soluble at 212° F. but it parts

with some of its acid at that temperature. At a low red heat, it is converted into the carbonate. From the analysis of Dr Wollaston, the crystals consist of one equivalent of potassa, two of acid, and one of water. I have likewise analyzed this salt, and obtained a similar result.

Dr Thomson, in his "First Principles," has described a sesquicarbonate, which was discovered by Dr Nimmo of Glasgow. Its crystals are composed of one equivalent of potassa, an equivalent and a half of carbonic acid, and six equivalents of water.

*Carbonate of Soda.*—The carbonate of soda of commerce is obtained by lixiviating the ashes of sea-weeds. The best variety is known by the name of *barilla*, and is derived chiefly from the *salsola soda* and *salicornia herbacea*. A very inferior kind, known by the name of *kelp*, is prepared from sea-weeds on the northern shores of Scotland. The purest barilla, however, though well fitted for making soap and glass, and for other purposes in the arts, always contains the sulphates and muriates of potassa and soda, and on this account is of little service to the chemist. A purer carbonate is prepared by heating a mixture of sulphate of soda, saw-dust, and lime, in a reverberatory furnace. By the action of the carbonaceous matter, the sulphuric acid is decomposed; its sulphur partly uniting with lime and partly being dissipated in the form of sulphurous acid, while the carbonic acid, which is generated during the process, unites with soda. The carbonate of soda is then obtained by lixiviation and crystallization. It is difficult to obtain this salt quite free from sulphuric acid.

The quantity of real carbonate in the soda of commerce may be conveniently estimated by its neutralizing power. One hundred grains of pure carbonate of soda is neutralized by 460 grains of sulphuric acid of density 1.141.

Carbonate of soda crystallizes in octahedrons with a rhombic base, the acute angles of which are generally truncated. The crystals effloresce on exposure to the air, and, when heated, dissolve in their water of crystallization. By continued heat, they are rendered anhydrous without loss of carbonic acid. They dissolve in about two parts of cold, and in rather less than their weight of boiling water, and the solution has a strong alkaline taste and reaction. According to Dr Thomson, the crystals are composed of 22 parts or one equivalent of carbonic acid, 32 parts or one equivalent of soda, and 90 parts or ten equivalents of water. The water of crystallization is apt to vary according to the temperature at which the crystals are formed.

*Bicarbonate of Soda.*—This salt is made by transmitting a current of carbonic acid gas through a solution of the carbonate, and is deposited in crystalline grains by evaporation. Though still alkaline, it is much milder than the carbonate, and far less soluble, requiring about ten times its weight of water at 60° F. for solution. It is decomposed partially at 212° F. and is converted into the carbonate by a red heat. It is composed, according to Thomson, of two equivalents of acid, one of the base, and one of water. This result I have confirmed by my own observation.

*Sesquicarbonate.*—This compound occurs native on the banks of the lakes of soda in the province of Sukena in Africa, whence it is exported under the name of *Trona*. It was first distinguished from the two other carbonates by Mr Phillips*, whose analysis corresponds

* Journal of Science, vol. vii.

with that of Klaproth. It consists of one equivalent of soda, an equivalent and a half of acid, and two equivalents of water.

*Carbonate of Ammonia.*—The only method of procuring this salt is by mixing dry carbonic acid over mercury, with twice its volume of ammoniacal gas. It is a dry white volatile powder, of an ammoniacal odour, and alkaline reaction. From the proportion of its constituents by volume, it is easy to infer that it is composed, by weight, of 22 parts or one equivalent of carbonic acid, and 17 parts or one equivalent of ammonia.

*Bicarbonate of Ammonia.*—This salt was formed by Berthollet, by transmitting a current of carbonic acid gas through a solution of the common carbonate of ammonia of the shops. On evaporating the liquid by a gentle heat, the bicarbonate is deposited in small six-sided-prisms, which have no smell, and very little taste. Berthollet ascertained that it contains twice as much acid as the carbonate.

*Sesquicarbonate of Ammonia.*—The common carbonate of ammonia of the shops, the *subcarbonas ammoniæ* of the pharmacopœia, is different from both these compounds. It is prepared by heating a mixture of one part of muriate of ammonia with one part and a half of the carbonate of lime, carefully dried. Double decomposition ensues during the process; muriate of lime remains in the retort, and the sesquicarbonate of ammonia is sublimed*. The carbonic acid and ammonia are, indeed, in proper proportion in the mixture for forming the real carbonate; but from the heat employed in the sublimation, part of the ammonia is disengaged in a free state.

The salt thus formed consists, according to the analysis of Mr Phillips, Dr Ure, and Dr Thomson, of 33 parts or an equivalent and a half of carbonic acid, of 17 parts or one equivalent of ammonia, and 9 parts or one equivalent of water. When recently prepared it is hard, compact, semi-transparent, of a crystalline texture, and pungent ammoniacal odour; but if exposed to the air, it loses weight rapidly, and is converted into an opake brittle mass, which is the bicarbonate.

*Carbonate of Baryta* occurs abundantly in the lead mines of the north of England, where it was discovered by Dr Withering, and has hence received the name of *Witherite.* It may be prepared by way of double decomposition, by mixing a soluble salt of baryta with any of the alkaline carbonates or bicarbonates. It is exceedingly insoluble in distilled water, requiring 4300 times its weight of water at 60° F. and 2300 of boiling water for solution; but when recently precipitated, it is dissolved much more freely by a solution of carbonic acid. It is highly poisonous.

*Carbonate of Strontia,* which occurs native at Strontian in Argyleshire, and is known by the name of *strontianite,* may be prepared in the same manner as carbonate of baryta. It is very insoluble in pure water, but is dissolved by an excess of carbonic acid.

*Carbonate of Lime.*—This salt is a very abundant natural production, and occurs under a great variety of forms; such as common limestone, chalk, marble, and Iceland spar, and in regular crystals. It may also be formed by precipitation. Though sparingly soluble in pure water, it is dissolved by carbonic acid in excess. On this ac-

* The products of this decomposition are, strictly speaking, sesquicarbonate of ammonia, water, and chloride of calcium. The sesquicarbonate and water sublime together, and *chloride of calcium* is left in the retort. B.

count the spring water of limestone districts always contains carbonate of lime, which is deposited when the water is boiled.

*Carbonate of Magnesia.*—This salt is easily prepared by adding carbonate of potassa in slight excess to a hot solution of sulphate of magnesia, and edulcorating the precipitated carbonate with warm water. It requires 2493 parts of cold, and 9000 of hot water for solution. It is so soluble in an excess of carbonic acid, that the sulphate of magnesia is not precipitated at all in the cold by the alkaline bicarbonates, or by the sesquicarbonate of ammonia. On allowing a solution of carbonate of magnesia in carbonic acid to stand in an open vessel, minute crystals are deposited, which consist of 42 parts or one equivalent of the carbonate, and 27 parts or three equivalents of water. (Dr Henry and Berzelius.)

The native carbonate of magnesia, according to the analysis of Dr Henry and Stromeyer, is similar in composition to the precipitated carbonate.

*Carbonate of Iron.*—Carbonic acid does not form a definite compound with peroxide of iron, but with the protoxide it constitutes a salt which is an abundant natural production, occurring sometimes massive, and at other times crystallized in rhomboids or hexagonal prisms. This protocarbonate of iron is contained also in most of the chalybeate mineral waters, being held in solution by free carbonic acid; and it may be formed by mixing an alkaline carbonate with the protosulphate of iron. When prepared by precipitation it attracts oxygen rapidly from the atmosphere, and the protoxide of iron, passing into the state of peroxide, parts with carbonic acid. For this reason, the carbonate of iron of the pharmacopœia is of a red colour, and consists chiefly of the peroxide.

*Carbonate of Copper.*—The beautiful green mineral, called *malachite*, is a carbonate of the peroxide of copper; and a similar compound may be formed from the persulphate by double decomposition, or by exposing metallic copper to air and moisture. According to the analysis of malachite by Mr Phillips, this mineral is composed of 80 parts or one equivalent of the peroxide of copper, one equivalent of carbonic acid, and one equivalent of water. (Journal of Science, vol. iv.)

The blue pigment, called *verditer*, said to be prepared by decomposing nitrate of copper by chalk, is an impure carbonate*.

*Carbonate of Lead.*—This salt, which is the *white lead* or *ceruse* of painters, occurs native, but may be obtained by double decomposition. It is prepared for the purposes of commerce by exposing coils of thin sheet lead to the vapour of vinegar, when, by the action of the acid fumes, the lead is both oxidized and converted into a carbonate.

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* On the composition and preparation of this pigment, the reader may consult the remarks of Mr Phillips in the essay quoted in the text.

## SECTION VI.

### *SALTS OF THE HYDRACIDS.*

By the expression *salts of the hydracids* is meant those saline compounds, the acid of which contains hydrogen as one of its elements. These salts owing to the peculiar constitution of their acid, have certain common properties, and may, therefore, be described advantageously in the same section. Many of the circumstances relative to them have already been mentioned in sufficient detail, partly in the remarks introductory to the study of the metals, (page 275,) and partly in the description of the individual metals themselves. I shall, for this reason, describe the salts of the hydracids chiefly in a general manner, giving a particular description of those compounds only, which are possessed of some peculiar interest.

Most of the salts which are composed of a hydracid and a metallic oxide are so constituted, that the oxygen of the oxide contains a quantity of oxygen precisely sufficient for forming water with the hydrogen of the acid. This is true of all the neutral compounds containing a protoxide, without exception, and it likewise holds good in many other cases. Thus, in the soluble muriate of the peroxide of iron, the oxide, which contains an equivalent and a half of oxygen, is united with an equivalent and a half of acid; and in the soluble permuriate of copper, the oxide, which contains two equivalents of oxygen, is united with two equivalents of acid.

The elements of the salts of the hydracids, as mentioned at page 275, are very prone to arrange themselves in a new order. All these salts are exposed to the action of two divellent and three quiescent affinities. In the muriate of soda, for example, the forces which tend to prevent a change, are the attraction of sodium for oxygen, of chlorine for hydrogen, and of muriatic acid for soda; while the opposite affinities are the attraction of chlorine for sodium and of hydrogen for oxygen. The latter always preponderate when heat is employed, because the volatility of water favours the production of that fluid; and in many instances the affinities appear so nicely balanced, that the cohesion of one of the compounds is sufficient to influence the result, as is exemplified by muriate of soda, which, in the act of crystallizing, is converted into chloride of sodium.

## *Muriates or Hydrochlorates.*

Most of the salts of muriatic acid are soluble in water, and some of them exist only in a state of solution. They are distinguished from other salts by forming the white insoluble chloride of silver, when mixed with the nitrate of that base, and by being decomposed with disengagement of muriatic acid fumes by strong sulphuric acid. The decomposition of the muriates, owing to the volatile nature of their acid, is effected by the phosphoric and arsenic acids at the temperature of ebullition.

*Muriates of Potassa and Soda.*—These salts exist only in a state of solution, and are frequently contained in mineral springs. The muriate of soda, as already mentioned in the section on sodium, is the chief constituent of sea-water.

*Muriate of Ammonia.*—This salt, the *sal ammoniac* of commerce, was formerly imported from Egypt, where it is procured by sublimation from the soot of camel's dung; but it is now manufactured in Europe by several processes. The most usual method is to decompose sulphate of ammonia by the muriate either of soda or magnesia. Double decomposition ensues, giving rise in both cases to muriate of ammonia, and to sulphate of soda, when the muriate of that base is used, or to sulphate of magnesia, when the muriate of magnesia is employed. The sal ammoniac is afterwards obtained in a pure state by sublimation. Sulphate of ammonia may be conveniently procured for this purpose, either by lixiviating the soot of coal, which contains that salt in considerable quantity; or by digesting the impure carbonate of ammonia, procured by exposing bones and other animal matters to a red heat, with gypsum, so as to form an insoluble carbonate of lime, and a soluble sulphate of ammonia.

Muriate of ammonia has a pungent saline taste, and is soluble in three parts of water at 60° F, causing a considerable reduction of temperature during the solution. Boiling water dissolves about an equal weight, and the solution deposites crystals in cooling. At a temperature below redness, it sublimes without fusing or undergoing any change in composition, and condenses on cool surfaces as an anhydrous salt, which attracts humidity in a moist atmosphere, but if pure is not deliquescent.

When muriatic acid gas is mixed with an equal volume of ammonia, both gases disappear entirely, and pure muriate of ammonia results. It hence follows that this salt is composed by weight of 37 parts or one equivalent of muriatic acid, and 17 parts or one equivalent of ammonia.

*Muriate of Baryta.*—This compound is best formed by dissolving carbonate of baryta, either native or artificial, in muriatic acid diluted with three parts of water. It may also be formed by the action of muriatic acid on the hydrosulphuret of baryta, (page 292;) or by heating sulphate of baryta with an equal weight of muriate of lime until fusion takes place, and then dissolving the muriate of baryta which is generated, and separating it by means of a filter from the sulphate of lime.

Muriate of baryta, when its solution is gently evaporated, crystallizes readily in flat rectangular plates, bevelled at the edges, much resembling crystals of heavy spar. The crystals, according to Thomson, consist of 115 parts or one equivalent of muriate of baryta, and 9 parts or one equivalent of water. On heating the crystals to redness, two equivalents of water are expelled, and 106 parts or one equivalent of the chloride of barium are left. The crystals, therefore, may be regarded as chloride of barium with two equivalents of water of crystallization. The fact, noticed by Mr Graham, that the pulverized crystals lose two equivalents of water in a very dry atmosphere, and recover them again in a moist one, is very favourable to this opinion.

The crystallized muriate of baryta is insoluble in pure alcohol. It requires about two and a half times its weight of water at 60° F. for solution, and is much more soluble in boiling water. The crystals are permanent in the air.

This salt is much employed as a reagent in chemistry.

*Muriate of strontia* is made in the same manner as muriate of baryta, from which it is distinguished by forming prismatic crystals, by its solubility in alcohol, and by imparting a red tint to flame. The crystals consist of one equivalent of muriate of strontia, and eight equivalents of water; and when heated to redness, nine equivalents of

water are expelled, and one equivalent of the chloride of strontium remains.

The crystallized muriate attracts humidity from a moist atmosphere, but, if pure, it is permanent in a moderately dry air. The crystals are exceedingly soluble in boiling water, and require for solution about twice their weight of water at 60° F.

*Muriate of lime* is formed by neutralizing muriatic acid with pure marble. The salt is very soluble both in water and alcohol, and deliquesces with rapidity even in a dry atmosphere. It crystallizes, though with considerable difficulty, in prisms, which consist, according to Thomson, of one equivalent of muriate of lime, and six equivalents of water. When heated, seven equivalents of water are expelled and a chloride remains. It may of course be regarded as chloride of calcium, with seven equivalents of water of crystallization.

The crystallized muriate is the compound which produces such an intense degree of cold when mixed with snow. It is prepared for this purpose by evaporating the solution until a drop of it on falling upon a cold saucer becomes solid.

*Muriate of magnesia* exists in many mineral springs, and is contained abundantly in sea-water. When muriate of soda is separated from sea-water by crystallization, an uncrystallizable liquid, called *bittern*, is left, which consists chiefly of muriate of magnesia, and is much employed in the manufacture of sal ammoniac for decomposing sulphate of ammonia.

Muriate of magnesia has a bitter taste, is highly soluble in alcohol and water, and deliquesces with rapidity in the open air. When heated to redness, it loses a portion of its acid as well as water.

*Muriate of iron.*—When iron is dissolved in dilute muriatic acid, a muriate of the protoxide is generated, which yields pale green-coloured crystals when the solution is concentrated by evaporation. This salt is much more soluble in hot than in cold water, and is not deliquescent. It absorbs oxygen with rapidity from the air, forming a soluble muriate of the peroxide. When boiled with a little nitric acid, a soluble muriate of the peroxide is also generated, which is of a red colour, crystallizes with difficulty, deliquesces on exposure to the air, and is dissolved by alcohol. It is composed of one equivalent of the peroxide, and an equivalent and a half of muriatic acid, being a sesquimuriate.

The black oxide is also dissolved by muriatic acid, forming a dark coloured solution, which may be regarded as a mixture of the muriates of the peroxide and protoxide of iron. (Page 318.)

## Hydriodates.

Hydriodic acid unites with the alkalies and alkaline earths, and with the oxides of manganese, zinc, and iron. With several of the metallic oxides, it does not enter into combination. Thus on mixing the hydriodate of potassa with a salt of mercury or silver, the iodides of these metals are deposited. With the acetate of lead, a yellow compound is thrown down, which is an iodide of lead.

The most direct method of forming the hydriodates of the alkalies and alkaline earths, all of which are soluble in water, is by neutralizing those bases with hydriodic acid. The hydriodates of iron and zinc may be made by digesting small fragments of those metals with water in which iodine is suspended.

All the hydriodates are decomposed by sulphuric and nitric acids, or

by chlorine, the hydriodic acid being deprived of hydrogen, and the iodine set at liberty. (Page 214.) They are not decomposed by exposure to the air.

The only hydriodates which have hitherto been found native are those of potassa and soda, the sources of which have already been mentioned in the section on iodine. Of these salts, the hydriodate of potassa is the most common.

*Hydriodate of Potassa.*—This salt, which is the only hydriodate of importance, exists only in solution; for it is converted in the act of crystallizing into iodide of potassium. It is exceedingly soluble in boiling water, and requires only two-thirds of its weight of water at 60° F. for solution. It is dissolved freely by alcohol; and when a saturated, hot, alcoholic solution is set aside to cool, iodide of potassium is deposited in cubic crystals. A solution of hydriodate of potassa is capable of dissolving a large quantity of iodine, a property which is common to all the hydriodates.

The hydriodate of potassa is easily made by neutralizing hydriodic acid with pure potassa; but in preparing a considerable quantity of the salt, as for medical use, it is desirable to dispense with the preliminary step of making the acid. With this intention the following method, which I have described in the Edinburgh Medical and Surgical Journal for July 1825, may be employed with advantage. The process consists in adding to a hot solution of pure potassa as much iodine as it is capable of dissolving, by which means a deep brownish-red coloured fluid is formed, consisting of the iodate and hydriodate of potassa, together with a large excess of free iodine. Through this solution a current of sulphuretted hydrogen gas is transmitted, until the free iodine and iodic acid are converted into hydriodic acid, changes which may be known to be accomplished by the liquid becoming quite limpid and colourless. The solution is then gently heated in order to expel any excess of sulphuretted hydrogen, and, after being filtered, the free hydriodic acid is exactly neutralized by pure potassa.

A still easier process has been proposed, which consists in adding iodine to a solution of hydrosulphate of potassa, or the common *hepar sulphuris* of the Pharmacopœia, (page 273) until the potassa is exactly neutralized. The hydriodate is then formed at once, without the necessity of a current of sulphuretted hydrogen gas.

## *Hydrobromates.*

The salts of hydrobromic acid have as yet been but partially examined, and the chief facts known respecting them have already been mentioned in the section on bromine.

## *Hydrofluates.*

Hydrofluoric acid unites readily with the pure alkalies, yielding soluble hydrofluates, which are converted into metallic fluorides by the action of heat. The neutral hydrofluates of the alkalies, those namely that contain one equivalent of acid and one equivalent of base, have an alkaline reaction. It may be doubted if this acid can unite at all with the alkaline earths; for it yields with them insoluble compounds, which have all the characters of metallic fluorides. The same remark applies to the action of hydrofluoric acid on the earths, with the exception of alumina and zirconia, which form soluble hydrofluates.

The salts of hydrofluoric acid are recognised by forming with mu-

riate of lime, a white gelatinous precipitate, which yields hydrofluoric acid when heated with concentrated sulphuric acid.

It is doubtful if any hydrofluate exists ready formed in the mineral kingdom. Four minerals may be enumerated as such; namely, the *topaz* or the double hydrofluate of silica and alumina, the hydrofluate of cerium, double hydrofluate of cerium and yttria, and *cryolite* or the double hydrofluate of alumina and soda. It is probable, however, that these compounds, like fluor spar, are metallic fluorides.

*Hydrofluate of Potassa.*—Potassa unites with hydrofluoric acid in two proportions, forming a hydrofluate and bihydrofluate; the former of which consists of one, and the latter of two, equivalents of acid, united with one equivalent of potassa. The hydrofluate, which has an alkaline reaction, is best prepared by supersaturating carbonate of potassa with hydrofluoric acid, evaporating the solution to dryness, and expelling the excess of acid by heat. The residue has a sharp saline taste, is deliquescent, and crystallizes with difficulty; but when evaporated at a temperature between 95° and 104°, it forms cubic crystals. These crystals, like the salt after being heated, are most probably fluoride of potassium.

The bihydrofluate is easily procured by adding to hydrofluoric acid a quantity of potassa insufficient for neutralizing it completely, and concentrating the solution. By slow evaporation it yields rectangular tables, the lateral edges of which are bevelled. This salt has an acid reaction, is soluble in water, and decomposed by heat.

*Hydrofluate of Soda.*—The neutral and acid hydrofluates of soda may be formed in the same manner as the preceding salts. The acid hydrofluate consists of one equivalent of base and two of the acid, possesses a sharp and purely sour taste, is but sparingly soluble in cold water, and crystallizes in transparent rhombohedrons. The neutral hydrofluate is sparingly soluble in water, and its solubility is not increased by elevation of temperature. It is almost completely insoluble in alcohol. It commonly crystallizes in cubes like chloride of sodium, but assumes the form of an octahedron when carbonate of soda is present.

The neutral and acid hydrofluates of lithia are sparingly soluble in water.

The neutral *hydrofluate of ammonia* may be prepared by mixing in a platinum crucible 1 part of sal ammoniac and 2 1-4 parts of fluoride of sodium, both in fine powder and quite dry, and applying a gentle heat with a spirit lamp. The hydrofluate of ammonia sublimes, and condenses in small prisms on the lid of the crucible, if kept cool, without any admixture of muriate of ammonia. Chloride of sodium is generated at the same time.

This salt is permanent in the air, slightly soluble in alcohol, and copiously dissolved by water. It corrodes glass vessels even in its dry state. In solution it gradually parts with ammonia, and is converted into a deliquescent bihydrofluate.

It is doubtful if the alkaline earths combine at all with hydrofluoric acid. On digesting recently precipitated carbonate of baryta in an excess of this acid, carbonic acid is gradually evolved, and a compound is formed, which appears to be a fluoride of barium. It is very slightly soluble in water and hydrofluoric acid; but it is dissolved freely by muriatic acid, and ammonia added to the solution causes a precipitate, which is a compound of fluoride and chloride of barium. A similar substance is formed on mixing a solution of muriate of baryta with an alkaline hydrofluate.

On digesting newly precipitated carbonate of lime in an excess of

hydrofluoric acid, a granular fluoride of calcium is generated. It is insoluble in water and hydrofluoric acid, and is very slightly dissolved by muriatic acid. It may also be formed by double decomposition; but it then forms a translucid jelly, which fills up the pores of a filter, and is therefore washed with difficulty. This compound appears to be identical with the beautiful mineral, commonly known by the name of *fluor* or *Derbyshire spar*. This mineral frequently accompanies metallic ores, especially those of lead and tin; and it often occurs crystallized either in cubes or some of its allied forms. The crystals found in the lead mines of Derbyshire are remarkable for the largeness of their size, the regularity of their form, and the variety and beauty of their colours. It is employed in forming vases, as a flux in metallurgic processes, and in the preparation of hydrofluoric acid. The nature and composition of this substance were considered on a former occasion. (Page 225.)

For an account of the action of hydrofluoric acid on other metallic oxides, I may refer to an essay of Berzelius on this subject. (Annals of Philosophy, xxiv. 335.)

## *Hydrosulphurets or Hydrosulphates.*

Sulphuretted hydrogen forms soluble salts with the alkalies and alkaline earths, most of which are capable of crystallizing. With the alkalies, indeed, if not with other bases, this acid unites in two proportions, forming a hydrosulphate and a bihydrosulphate. It may be doubted if sulphuretted hydrogen is capable of uniting with any of the oxides of the common metals; for when their salts are mixed with the hydrosulphate of potassa, a precipitate takes place, which, in most, if not in all cases, is the sulphuret of a metal, and not the hydrosulphate of its oxide. Thus, by the action of the hydrosulphate of potassa on the nitrates of lead, copper, bismuth, silver, or mercury, nitrate of potassa is formed, water is generated, and a metallic sulphuret subsides. The precipitates occasioned by hydrosulphate of potassa in a salt of iron, zinc, and manganese, may also be regarded as sulphurets; for though sulphuric acid decomposes these compounds with evolution of sulphuretted hydrogen, it does not follow that that acid had previously existed in them.

As sulphuretted hydrogen is a weak acid, and naturally gaseous, its salts are decomposed by most other acids, such as the sulphuric, muriatic, and acetic acids, with disengagement of sulphuretted hydrogen gas, a character by which all the hydrosulphates are easily recognised. They are decomposed, likewise, by chlorine and iodine, with separation of sulphur, and formation of a muriate or hydriodate. When recently prepared, they form solutions which are colourless, or nearly so; but on exposure to the air, oxygen gas is absorbed, a portion of its acid is deprived of its hydrogen, and a sulphuretted hydrosulphate of a yellow colour is generated. By continued exposure, the whole of the sulphuretted hydrogen is decomposed, water and hyposulphurous acid being produced.

The hydrosulphates of baryta and strontia, prepared by dissolving the sulphurets of barium and strontium in water, are sometimes used in preparing the salts of those bases. The hydrosulphates of potassa and ammonia are employed as reagents.

*Hydrosulphate of Potassa.*—This salt is made by transmitting a current of sulphuretted hydrogen gas into a solution of pure potassa, contained in a Woulfe's apparatus, and continuing the operation as long as the gas is absorbed. When all the alkali is combined with

sulphuretted hydrogen, it is no longer able to precipitate a salt of magnesia. If the alkali is completely saturated with the gas, the resulting compound, though it has still an alkaline reaction, is a bihydrosulphate. This salt has an alkaline bitter taste, and crystallizes in six-sided prisms, which are deliquescent and soluble in alcohol as well as water.

*Hydrosulphate of Ammonia.*—This salt is made in the same manner as the preceding compound. It may be procured in white acicular crystals by mixing together sulphuretted hydrogen and ammoniacal gases in a dry vessel. As the crystals are very volatile, the vessel in which the combination is effected should be kept cool by ice.

*Hydroseleniates.*—These salts have been little examined, owing to the scarcity of selenium. The researches of Berzelius have demonstrated, however, that hydroselenic acid forms with the alkalies soluble compounds, which are very analogous in their chemical relations to the hydrosulphates, and which precipitate the salts of the common metals, giving rise in most, if not in all cases, to the formation of a metallic seleniuret.

## *Hydrocyanates.*

Hydrocyanic acid unites with alkalies and alkaline earths, and probably with several other bases; but these compounds have as yet been studied in a very imperfect manner. The hydrocyanate of potassa is the best known. It is generated by the decomposition of water when cyanuret of potassium is put into that fluid, and may be made directly by mixing hydrocyanic acid with a solution of potassa. M. Robiquet recommends that it should be prepared by exposing ferrocyanate of potassa to a long continued red heat, by which means the ferrocyanic acid is decomposed, and a dark mass, consisting of the cyanuret of potassium, mixed with charcoal and iron, remains in the crucible. This process succeeds well if carefully performed; but it is difficult to destroy the whole of the ferrocyanic acid, without decomposing at the same time the cyanuret of potassium. If the decomposition of the ferrocyanate is complete, the residue should form a colourless solution, which does not produce Prussian blue with a salt of the peroxide of iron.

The hydrocyanate of potassa appears to exist only in solution; for when evaporated to dryness, it is converted into cyanuret of potassium, a compound which is far less liable to spontaneous decomposition than hydrocyanic acid, and is capable of supporting a very high temperature in close vessels without change. It is deliquescent, and highly soluble in water. The solution gives a green colour to violets, and has an alkaline taste, accompanied with the flavour and a faint odour of hydrocyanic acid. It is decomposed by nearly all the acids, even by the carbonic, and on this account should be preserved in well closed vessels. It acts upon the animal system in the same manner as hydrocyanic acid, and MM. Robiquet and Villermé have proposed its employment in medical practice, as being more uniform in strength, and less prone to decomposition, than hydrocyanic acid. (Jour. de Physiologie, vol. iii.)

## *Ferrocyanates.*

The neutral ferrocyanates, so far as is known, appear to be formed in the same manner as the salts of the hydracids in general; namely, the hydrogen of the acid is in exact proportion for forming water with

the oxygen of the salifiable base with which it is united. Thus ferrocyanate of potassa is composed of one equivalent of ferrocyanic acid, which contains two of hydrogen, (page 260) and two equivalents of potassa. With the alkalies and alkaline earths, this acid forms soluble compounds; but it precipitates nearly all the salts of the common metals, giving rise either to the ferrocyanate of an oxide or the ferrocyanuret of a metal.

*Ferrocyanate of Potassa.*—This salt, sometimes called *triple prussiate of potassa*, is prepared by digesting pure ferrocyanate of the peroxide of iron in potassa until the alkali is neutralized, by which means the peroxide of iron is set free, and a yellow liquid is formed, which yields crystals of the ferrocyanate of potassa by evaporation. This salt is made on a large scale in the arts by igniting dried blood or other animal matters, such as hoofs and horns, with potash and iron. By the mutual reaction of these substances at a high temperature, the ferrocyanuret of potassium, consisting of one equivalent of the radical of ferrocyanic acid, (page 260,) and two equivalents of potassium, is generated. Such at least is inferred to be the product; for on digesting the residue in water, a solution of the ferrocyanate of potassa is obtained.

Ferrocyanate of potassa is a perfectly neutral salt, which is soluble in less than its own weight of water, and forms large transparent, four-sided tabular crystals, derived from an acute rhombic octahedron, the apices of which are deeply truncated. The colour of the salt is lemon-yellow; it is inodorous, has a slightly bitter taste, but quite different from that of hydrocyanic acid, and is permanent in the air. When heated to 212° F. or even below that temperature, each equivalent of the salt parts with three equivalents of water, leaving one equivalent of the ferrocyanuret of potassium. The water, indeed, is disengaged with such facility, that Berzelius regards the crystals as consisting of the ferrocyanuret of potassium combined with three equivalents of water of crystallization. (An. de Ch. et de Ph. vol. xv.) On heating the dry compound to full redness in close vessels, decomposition takes place, nitrogen gas is disengaged, and cyanuret of potassium mixed with carburet of iron remains in the retort.

Very great diversity of opinion prevails respecting the atomic constitution of this salt. There is good reason to believe from the experiments of Berzelius, Phillips, and others, that one equivalent of the crystallized salt contains the following substances:—

| | | |
|---|---|---|
| Cyanogen . . | 78 | or three equivalents. |
| Potassium . | 80 | two equivalents. |
| Iron . . | 28 | one equivalent. |
| Hydrogen . . | 3 | three equivalents. |
| Oxygen . . | 24 | three equivalents. |
| | 213 | |

Its solution in water has all the properties that may be expected from the presence of ferrocyanic acid and potassa, and I shall accordingly regard it, when in that state, as containing both these substances. In the form of crystals, it is perhaps more simple to consider it with Berzelius as a double cyanuret of iron and potassium, with water of crystallization. The reader will find a discussion of this subject in the Philosophical Magazine and Annals, i. 110, by Mr Phillips.

The ferrocyanate of potassa is employed in the preparation of several compounds of cyanogen, and as a reagent for detecting the presence of iron and other substances.

*Ferrocyanate of Baryta* is prepared by digesting purified Prussian blue with a solution of pure baryta. It is soluble in water, and forms yellow crystals by evaporation. It is used in the formation of ferrocyanic acid.

When ferrocyanate of potassa is mixed in solution with a salt of lead, a white precipitate subsides, which Berzelius has proved to be similar in composition to the ferrocyanuret of potassium, consisting of one equivalent of the radical of ferrocyanic acid, and two equivalents of lead. With salts of mercury and silver, analogous compounds, likewise of a white colour, are generated. With a per-salt of copper, the ferrocyanate of potassa causes a brownish-red precipitate, which appears to be the ferrocyanate of the peroxide of copper.

*Ferrocyanate of the peroxide of iron*, which is formed by mixing ferrocyanate of potassa with a per-salt of iron in slight excess, and washing the precipitate with water, is characterized by an intensely deep blue colour, and is the basis of the beautiful pigment called *Prussian blue*. It is insipid and inodorous, insoluble in water, and is not decomposed by dilute muriatic or sulphuric acid. Concentrated muriatic acid, by the aid of heat, separates the acid, and strong sulphuric acid renders it white—a change, the nature of which has not been explained. The alkalies and alkaline earths decompose it readily, uniting with the ferrocyanic acid and separating the peroxide of iron. The peroxide of mercury, as already mentioned, (page 360) effects the complete decomposition of the salt, forming bicyanuret of mercury. Very complicated changes are produced by an elevated temperature. On heating the ferrocyanate to redness in a close vessel, a considerable quantity of water and carbonate of ammonia, together with a small portion of hydrocyanate of ammonia, are generated; while a carburet of iron remains in the retort—phenomena which, in conjunction with the facts above stated, leave no doubt of this compound containing ferrocyanic acid and peroxide of iron. The precise proportion of its constituents has not been satisfactorily determined; but it most probably consists of one equivalent of the peroxide, and an equivalent and a half of the acid*.

Prussian blue, the discovery of which was made in 1710, has been studied by several chemists, especially by Proust, (An. de Chimie, lx.) and by Berzelius, Porrett, and Robiquet, to whose essays I referred while describing the ferrocyanic acid. The colouring matter of this pigment is ferrocyanate of the peroxide of iron, which is mixed with alumina and peroxide of iron, together with the subsulphates of one or both of those bases. It is prepared by heating to redness dried blood, or other animal matters, with an equal weight of pearlash,

* In this statement, Dr Turner does not appear to have adverted to the fact that ferrocyanic acid contains two equivalents of hydrogen. It is altogether probable, that in Prussian blue, the acid and base are united in such proportions, that the hydrogen of the former and the oxygen of the latter are in the proper ratio to form water. Now one equivalent of peroxide of iron contains an equivalent and a half of oxygen, and it would require three-fourths of an equivalent of the acid, supposing it to unite with a quantity of the latter, containing an equivalent and a half of hydrogen. Doubling these quantities, the probable proportions would be, two equivalents of peroxide of iron, and an equivalent and a half of the acid. B.

until the mixture has acquired a pasty consistence. The residue, which consists chiefly of cyanuret of potassium and carbonate of potassa, is dissolved in water, and after being filtered, is mixed with a solution of two parts of alum and one part of the protosulphate of iron. A dirty greenish precipitate ensues, which absorbs oxygen from the atmosphere, and passes through different shades of green and blue, until at length it acquires the proper colour of the pigment.

The chemical changes which take place in this process are of a complicated nature. The precipitate, which is at first thrown down, is occasioned by the potassa, and consists chiefly of alumina and the protoxide of iron. The ferrocyanic acid is generated by the protoxide reacting upon some of the hydrocyanic acid, so as to form water and cyanuret of iron, the latter of which then unites with undecomposed hydrocyanic acid. The ferrocyanic acid, thus produced, combines with oxide of iron; and when the latter has attained its maximum of oxidation, the compound acquires its characteristic blue tint. Dr Thomson, knowing the protoxide to be necessary to the success of the operation, concludes that this oxide enters into the composition of Prussian blue; but here this acute chemist is certainly in error. The only use of the protoxide of iron is to convert the hydrocyanic into ferrocyanic acid; a purpose for which its presence is essential, because the peroxide of iron does not produce this effect, or at least in a very slow and imperfect manner. In every good specimen of Prussian blue which I have examined, the ferrocyanic acid was in combination with the peroxide of iron only.

*Sulphocyanates.*—The salts of sulphocyanic acid have been chiefly studied by Mr Porrett and Berzelius. The sulphocyanate of potassa, which is the most interesting and the best known of these compounds, is prepared by heating ferrocyanate of potassa with sulphur, a process first proposed by Grotthus, and since modified by M. Vogel and myself. The most convenient method of performing it is to mix the ferrocyanate, in fine powder, with an equal weight of sulphur, and to place the mixture, contained in a porcelain capsule, just above a pan of burning charcoal, so that it may be exposed to a very strong heat, but short of redness. The mixture is speedily fused, takes fire, and burns briskly for one or two minutes, during which it should be well stirred. The combustion then ceases spontaneously, and the dark coloured residue, consisting of unburned sulphur, sulphocyanuret of potassium, and sulphuret of iron, on being dissolved in water and filtered, yields a very pure and neutral sulphocyanate of potassa. To insure the decomposition of all the ferrocyanate of potassa, the mass may be allowed to remain in a fused condition for a few minutes after the combustion has ceased, previous to withdrawing it from the fire.

In this process the iron and cyanogen of the ferrocyanate combine with separate portions of sulphur, forming a sulphuret of iron and a bisulphuret of cyanogen, the latter of which unites with potassium. On the addition of water, a portion of that liquid is decomposed, and sulphocyanate of potassa is generated.

Sulphocyanate of potassa (and most of the salts of this group have probably a similar constitution,) contains one equivalent of the acid, and one equivalent of the oxide; so that the oxygen and hydrogen are in due proportion for the production of water. This salt, indeed, exists only in a liquid state; for the crystals which are deposited from a concentrated solution, when separated from the adhering moisture by bibulous paper, do not contain either water or its ele-[illegible] but are a pure sulphocyanuret of potassium. The crystals are

very deliquescent on exposure to the air, and dissolve freely in water, yielding a solution which is quite neutral. In form, taste, and fusibility, they are very analogous to nitre.

The sulphocyanate of potassa is employed in preparing sulphocyanic acid, and as a test for detecting the presence of the peroxide of iron.

# PART III.

## *ON ORGANIC CHEMISTRY.*

THE department of organic chemistry comprehends the history of those compounds which are solely of animal or vegetable origin, and which are hence called organic substances. These bodies, viewed collectively, form a remarkable contrast with those of the mineral kingdom. Such substances in general are characterized by containing some principle peculiar to each. Thus the presence of nitrogen in the nitric, and of sulphur in the sulphuric acid, establishes a wide distinction between these substances; and although in many instances two or more inorganic bodies consist of the same elements, as is exemplified by the compounds of sulphur and oxygen, or of nitrogen and oxygen, they are always few in number, and distinguished by a well-marked difference in the proportion in which they are united. The products of animal and vegetable life, on the contrary, consist essentially of the same elementary principles, the number of which is very limited. They are nearly all composed of carbon, hydrogen, and oxygen, in addition to which some of them contain nitrogen. Besides these, portions of phosphorus, sulphur, iron, silica, potassa, lime, and other substances of a like nature, may sometimes be detected; but their quantity is exceedingly minute, when compared with the principles above mentioned. In point of composition, therefore, most organic substances differ only in the proportion of their constituents, and on this account may not unfrequently be converted into one another.

The constitution of organic bodies is subject to the general laws of chemical union; but chemists are not agreed as to the mode in which they conceive the elements to be combined. Berzelius, for instance, is of opinion that the elements of organic substances do not form binary compounds in the same manner as the constituents of inorganic bodies, (Page 375), but are united indiscriminately with one another. Thus alcohol, which consists of three equivalents of hydrogen, one of oxygen, and two of carbon, is supposed by that chemist to consist of all these six equivalents, combined directly with each other, the oxygen belonging as much to the carbon as to the hydrogen. (Annals of Philosophy, vol. iv.) This opinion, however, is not universally adopted. Gay-Lussac, for instance, regards alcohol as a compound of olefiant gas and water, a view which is not only justified by the number of equivalents contained in that compound, but which, as I conceive, harmonizes with the constitution of other bodies better than that of Berzelius. It may, therefore, be admitted as probable, that the elements of organic substances are arranged in a similar manner.

Organic substances owing to the energetic affinities with which their elements are endowed, are very prone to spontaneous decomposition. The prevailing tendency of carbon and hydrogen is to appropriate to themselves so much oxygen as shall convert them into carbonic acid and water; and hence, in whatever manner these three elements may be mutually combined in a vegetable substance, they are always disposed to resolve themselves into the compounds just mentioned. If at the time this change occurs there is an insufficient supply of oxygen to oxidize the hydrogen and carbon completely, then in addition to carbonic acid and water, carbonic oxide and carburetted hydrogen gases will probably be generated. One or both of these combustible products must in every case be formed, except when oxygen is freely supplied from extraneous sources; because organic bodies are so constituted, that their oxygen is never in sufficient quantity for converting the carbon into carbonic acid, and the hydrogen into water.

If substances composed of oxygen, hydrogen, and carbon, are liable to spontaneous decomposition, that tendency becomes much stronger, when, in addition to these elements, nitrogen is annexed. Other and powerful affinities are then superadded to those above enumerated, and especially that of hydrogen for nitrogen. A body which contains these principles is peculiarly liable to change, and the usual products are water, carbonic acid, and ammonia, the two latter, having a strong attraction for each other, being always in combination.

Another circumstance which is characteristic of organic products is the impracticability of forming them artificially by direct union of their elements. Thus no chemist has hitherto succeeded in causing oxygen, hydrogen, and carbon to unite directly so as to form gum or sugar. When these principles are made to combine by chemical means, they always give rise to the production of water and carbonic acid.

Animal and vegetable substances are all decomposed by a red heat, and nearly all are partially affected by a temperature far below ignition. When heated in the open air, or with substances which yield oxygen freely, they burn, and are converted into water and carbonic acid; but if exposed to heat in vessels from which atmospheric air is excluded, very complicated products ensue. A compound, consisting of carbon, hydrogen, and oxygen, yields water, carbonic acid, carbonic oxide, carburetted hydrogen of various kinds, and probably pure hydrogen. Besides these products, some acetic acid is commonly generated, together with a volatile oil which has a dark colour and burnt odour, and is hence called empyreumatic oil. An azotized substance, in addition to these, yields ammonia, cyanogen, and probably free nitrogen.

From the foregoing remarks, it appears that organic products are characterized by the following circumstances:—1st, by being composed of the same elements; 2d, by the facility with which they undergo spontaneous decomposition; 3d, by the impracticability of forming them by the direct union of their principles; and, 4th, by being decomposed at a red heat.

## *Vegetable Chemistry.*

All bodies which are of vegetable origin are termed vegetable substances. They are nearly all composed of oxygen, hydrogen, and carbon, and in a few of them nitrogen is likewise present. Every distinct compound which exists ready formed in plants, is called a *proximate* or *immediate principle* of vegetables. Thus sugar, starch, and gum are proximate principles. Opium, though obtained from a plant, is not

a proximate principle; but consists of several proximate principles, mixed more or less intimately with one another.

The proximate principles of vegetables are sometimes distributed over the whole plant, while at others they are confined to a particular part. The methods by which they are procured are very variable. Thus gum exudes spontaneously, and the saccharine juice of the maple tree is obtained by incisions made in the bark. In some cases a particular principle is mixed with such a variety of others, that a distinct process is required for its separation. Of such processes consists the *proximate analysis* of vegetables. Sometimes a substance is separated by mechanical means, as in the preparation of starch. On other occasions, advantage is taken of the volatility of a compound, or of its solubility in some particular menstruum. Whatever method is employed, it should be of such a nature as to occasion no change in the composition of the body to be prepared.

The reduction of the proximate principles into their simplest parts, constitutes their *ultimate analysis*. By this means chemists ascertain the quantity of oxygen, carbon, and hydrogen, present in any compound. The former method of performing this operation was by what is termed *destructive distillation;* that is, by exposing the compounds to a red heat in close vessels, and collecting all the products. So many different substances, however, are procured in this way, such as water, carbonic acid, carbonic oxide, carburetted hydrogen, and the like, that it is almost impossible to arrive at a satisfactory conclusion. A more simple and effectual method was proposed by Gay-Lussac and Thenard, in the second volume of their celebrated *Recherches Physico-Chimiques*. The object of their process, which is applicable to the ultimate analysis of animal, as well as vegetable substances, is to convert the whole of the carbon into carbonic acid, and the hydrogen into water, by means of some compound which contains oxygen in so loose a state of combination, as to give it up to those elements at a red heat.

The agent first employed by these chemists was chlorate of potassa. This substance, however, is liable to the objection that it not only gives oxygen to the substance to be analyzed, but is itself decomposed by heat. On this account it is now very rarely employed in ultimate analysis, the peroxide of copper, likewise proposed by Gay-Lussac and Thenard, having been substituted for it. This oxide, if alone, may be heated to whiteness without parting with oxygen; whereas it yields oxygen readily to any combustible substance with which it is ignited. It is easy, therefore, by weighing it before and after the analysis, to discover the precise quantity of oxygen which has entered into union with the carbon and hydrogen of the substance submitted to examination.

The ultimate analysis of organic bodies is one of the most delicate operations with which the analytical chemist can be engaged. The chief cause of uncertainty in the process arises from the presence of moisture, which is retained by some animal and vegetable substances with such force that it can be expelled only by a temperature which endangers the decomposition of the compound itself. The best mode of drying organic matters for the purpose, is by confining them with sulphuric acid under the exhausted receiver of an air-pump, and exposing them at the same time to a temperature of 212° F,—a method adopted by Berzelius, and for which a neat apparatus has been described by Dr Prout. (Annals of Philosophy, vol. vi. p. 272.) Another source of difficulty is occasioned by atmospheric air within the apparatus, owing to the presence of which nitrogen may be de-

tected in the products, without having been contained in the substance analyzed.

But though the ultimate analysis of organic substances is difficult in practice, in theory it is exceedingly simple. It consists in mixing three or four grains of the body to be analyzed with about two-hundred grains of the peroxide of copper, heating the mixture to redness in a glass tube, and collecting the gaseous products in a graduated glass jar over mercury. From the quantity of carbonic acid procured by measure, its weight may readily be inferred; (page 173); and from this, the quantity of carbonaceous matter is calculated, by recollecting that every 22 grains of the acid contain 16 of oxygen and 6 of carbon.

In order to ascertain the quantity of hydrogen, the gaseous products are transmitted through a tube filled with fragments of fused chloride of calcium, which absorbs all the watery vapour; and by its increase in weight indicates the precise quantity of that fluid generated. Every 9 grains of water thus collected correspond to 1 grain of hydrogen and 8 of oxygen.

If the quantity of oxygen contained in the carbonic acid and water corresponds precisely to that lost by the oxide of copper, it follows that the organic substance itself was free from oxygen. But if, on the other hand, more oxygen exists in the products than was lost by the copper, it is obvious that the difference indicates the amount of oxygen contained in the subject of analysis.

If nitrogen enters into the constitution of the organic substance, it will pass over in the gaseous state, mixed with carbonic acid. Its quantity may be ascertained by removing the carbonic acid by means of a solution of pure potassa.

It need scarcely be observed, that if the analysis has been successfully performed, the weight of the different products, added together, should make up the exact weight of the organic substance employed.

In analyzing an animal or vegetable fluid, the foregoing process will require a slight modification. If the fluid is of a fixed nature, it may be made into a paste with the oxide of copper, and heated in the usual manner. But if it is volatile, a given weight of its vapour is conducted over the peroxide of copper heated to redness in a glass tube.

The constitution of vegetable substances is not yet sufficiently known to admit of their being classified in a purely scientific order. The chief data hitherto furnished towards forming a systematic arrangement, are derived from a remarkable agreement between the composition and general properties of several vegetable compounds, first noticed by Gay-Lussac and Thenard. (Recherches, vol. ii.) From the ultimate analysis of a considerable variety of proximate principles, these chemists draw the three following conclusions:—1st, A vegetable substance is always acid, when it contains more than a sufficient quantity of oxygen for converting all its hydrogen into water; 2dly, It is always resinous, oily, or alcoholic, &c. when it contains less than a sufficient quantity of oxygen for combining with the hydrogen; and 3dly, it is neither acid nor resinous, but in a state analogous to sugar, gum, starch, or the woody fibre, when the oxygen and hydrogen, which it contains, are in the exact proportion for forming water. These laws, indeed, are not rigidly exact, nor do they include the vegetable products containing nitrogen; but for want of a better principle of classification, I shall follow M. Thenard in making them, to a certain extent, the basis of my arrangement. I shall accordingly arrange the proximate principles of plants in five divisions.

The first includes the vegetable acids; the second the vegetable alkalies; the third comprises those substances which contain an excess of hydrogen; the fourth includes those, the oxygen and hydrogen of which are in proportion for forming water; and the fifth comprehends those bodies which, so far as is known, do not belong to either of the other divisions.

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## SECTION I.

### *VEGETABLE ACIDS.*

Those compounds are regarded as vegetable acids which possess the properties of an acid, and are derived from the vegetable kingdom. These acids, like all organic principles, are decomposed by a red heat. They are in general less liable to spontaneous decomposition than other vegetable substances; a circumstance which probably arises from the large proportion of oxygen which they contain. They are nearly all decomposed by concentrated hot nitric acid, by which they are converted into carbonic acid and water.

### *Acetic Acid.*

The acetic acid exists ready formed in the sap of many plants, either free or combined with lime or potassa; it is generated during the destructive distillation of vegetable matter, and is an abundant product of the acetous fermentation.

Common vinegar, the acidifying principle of which is acetic acid, is commonly prepared in this country by fermentation from an infusion of malt, and in France from the same process taking place in weak wine. Vinegar, thus obtained, is a very impure acetic acid, containing the saccharine, mucilaginous, and other matters, existing in the fluid from which it is prepared. It is separated from these impurities by distillation. Distilled vinegar was formerly called *acetous acid*, on the supposition of its differing chemically from strong acetic acid; but it is now admitted that distilled vinegar is real acetic acid merely diluted with water, and commonly containing a small portion of empyreumatic oil, formed during the distillation, and from which it receives a peculiar flavour. It may be rendered stronger by exposure to cold, when a considerable part of the water is frozen, while the acid remains liquid.

The distilled vinegar, which is now generally employed for chemical purposes, is prepared by the distillation of wood, and is sold under the name of *pyroligneous acid*. When first made it is very impure, and of a dark colour, holding in solution tar and volatile oil; but it may be purified, at least in part, by digestion with animal charcoal and a second distillation, or by filtration through animal charcoal. The method employed for purifying it at Glasgow, where it is made in large quantity, has not to my knowledge been made public.

Concentrated acetic acid is best obtained by decomposing the acetates, either by sulphuric acid, or in some instances by heat. A convenient process is to distil acetate of potassa with half its weight of concentrated sulphuric acid, the recipient being kept cool by the

application of ice. The acid is at first contaminated with sulphurous acid; but by mixing it with a little peroxide of manganese, and redistilling, it is rendered quite pure. A strong acid may likewise be procured from the binacetate of copper by the sole action of heat. The acid when first collected has a greenish tint, owing to the presence of copper, from which it is freed by a second distillation. The density of the product varies from 1.056 to 1.08, the lightest acid being procured towards the end of the process. MM. Derosnes, indeed, have remarked that the liquid which passes over towards the end of the process is lighter than water, and contains very little acetic acid. On neutralizing the latter with pure solid potassa, and distilling by a gentle heat, they procured an ethereal fluid, to which they applied the term of *pyro-acetic ether*.

Strong acetic acid is exceedingly pungent, and even raises a blister when kept for some time in contact with the skin. It has a very sour taste and an agreeable refreshing odour. Its acidity is well marked, as it reddens litmus paper powerfully, and forms neutral salts with the alkalies. It is exceedingly volatile, rising rapidly in vapour at a moderate temperature without undergoing any change. Its vapour is inflammable, and burns with a white light. In its most concentrated form, it is a definite compound of one equivalent of water, and one equivalent of acid; and in this state it crystallizes when exposed to a low temperature, retaining its solidity until the thermometer rises to 50° F. It is decomposed by being passed through red-hot tubes; but owing to its volatility, a large quantity of it escapes decomposition.

Dr Prout* has established the singular fact, relative to the constitution of this acid, that its oxygen and hydrogen are in exact proportion to form water†, and that it contains 47.05 per cent of carbon. It may hence be inferred to consist of 24 parts or four equivalents of carbon, 24 parts or three equivalents of oxygen, and 3 of hydrogen. This would make the combining proportion of acetic acid 51, instead of 50 as stated by Dr Thomson.

The only correct mode of estimating the strength of acetic acid is by its neutralizing power. Its specific gravity is no criterion, as will appear from the following table. (Thomson's First Principles, vol. ii. p. 135.)

*Table exhibiting the Density of Acetic Acid of different Strengths.*

| *Acid.* | | *Water.* | *Sp. gr. at 60° F.* |
|---|---|---|---|
| 1 atom | + | 1 atom | 1.06296 |
| 1 | + | 2 | 1.07060 |
| 1 | + | 3 | 1.07084 |
| 1 | + | 4 | 1.07132 |
| 1 | + | 5 | 1.06820 |
| 1 | + | 6 | 1.06708 |
| 1 | + | 7 | 1.06349 |
| 1 | + | 8 | 1.05974 |
| 1 | + | 9 | 1.05794 |
| 1 | + | 10 | 1.05439 |

* Philosophical Transactions for 1827, p. 355.

† Gay-Lussac and Thenard established this fact as nearly as possible, by their analysis of acetic acid, reported in their *Recherches Physico-Chimiques*. The proportions of oxygen and hydrogen which they obtained are very nearly in the ratio to form water. It is true that Thenard in his *Traité* gives the oxygen as if in excess; but this state-

The acetic is distinguished from all other acids by its flavour, odour, and volatility. Its salts, which are called *acetates*, are all soluble in hot and most of them in cold water, are destroyed by a high temperature, and are decomposed by sulphuric acid.

*Acetate of Potassa.*—This salt is made by neutralizing carbonate of potassa with acetic acid, or by decomposing acetate of lime with sulphate of potassa. When cautiously evaporated, it forms irregular crystals, which are obtained with difficulty, owing to the deliquescent property of the salt. According to Dr Thomson, the crystals are composed of one equivalent of the neutral acetate of potassa, and two equivalents of water. It is commonly prepared for pharmaceutic purposes by evaporating the solution to dryness, and heating the residue so as to cause the igneous fusion. On cooling it becomes a white crystalline foliated mass, which is generally alkaline.

This salt is highly soluble in water, and requires twice its weight of boiling alcohol for solution.

Dr Thomson procured a binacetate by mixing acetic acid and carbonate of potassa in the proportion of two equivalents of the former to one of the latter. On confining the solution along with sulphuric acid under the exhausted receiver of an air-pump, the binacetate was deposited in large transparent flat plates. The crystals contain six equivalents of water, and deliquesce rapidly on exposure to the air.

*Acetate of Soda* is prepared in large quantity by manufacturers of pyroligneous acid by neutralizing the impure acid with chalk, and then decomposing the acetate of lime by sulphate of soda. It crystallizes readily by gentle evaporation, and its crystals, which are not deliquescent, are composed of 50 parts or one equivalent of acetic acid, 32 parts or one equivalent of soda, and 54 parts or six equivalents of water. (Berzelius and Thomson.) The form of its crystals is very complicated, and derived from an oblique rhombic prism. (Brooke.) When heated to 550° F, it is deprived of its water, and undergoes the igneous fusion without parting with any of its acid. At 600° F. decomposition takes place.

Acetate of soda is much employed for the preparation of concentrated acetic acid.

*Acetate of Ammonia* is made by neutralizing the common carbonate of ammonia with acetic acid. It crystallizes with difficulty in consequence of being deliquescent and highly soluble. It has been long used in medicine as a febrifuge under the name of *spirit of Mindererus.*

The *acetates of baryta, strontia, and lime* are of little importance. The former, which is occasionally employed as a reagent, crystallizes in irregular six-sided prisms terminated by dihedral summits, the primary form of which is a right rhomboidal prism. The latter crystallizes in very slender acicular crystals of a silky lustre, and is chiefly employed in the preparation of the acetate of soda.

Acetate of alumina is formed by adding acetate of lead to sulphate of alumina, when the sulphate of lead subsides and the acetate of alumina remains in solution. It is used by Dyers and Calico-printers as a basis or mordant.

*Acetate of Lead.*—This salt, long known by the names of sugar of

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ment is evidently made up in accordance with a former ratio for the composition of water, which is not at present admitted by the French chemist himself. *Thenard. Traité de Chimie, 5ème édition, tome iii, p.* 598. B.

lead (*saccharum Saturni*) and *cerussa acetata*, is made by dissolving either carbonate of lead or litharge in distilled vinegar. The solution has a sweet, succeeded by an astringent taste, does not redden litmus paper, and deposites shining acicular crystals by evaporation. When more regularly crystallized, it occurs in six-sided prismatic crystals, cleavable parallel to the lateral and terminal planes of a right rhombic prism, which may be regarded as its primary form. (Mr Brooke.) The crystals effloresce slowly by exposure to the air, and require about four times their weight of water at 60° F. for solution. They are composed, according to Berzelius and Thomson, of 50 parts or one equivalent of the acid, 112 parts or one equivalent of the protoxide of lead, and 27 parts or three equivalents of water.

The acetate of lead is partially decomposed, with formation of the carbonate of lead, by water which contains carbonic acid, or by exposure to the air; but a slight addition of acetic acid renders the solution quite clear.

This salt is much used in the arts, in medical and surgical practice as a sedative and astringent, and in chemistry as a reagent.

The *subacetate* of lead, commonly called *extractum Saturni*, is prepared by boiling one part of the neutral acetate, and two parts of litharge, deprived of carbonic acid by heat, with 25 parts of water.

This salt is less sweet and less soluble in water than the neutral acetate, has an alkaline reaction, and crystallizes in white plates by evaporation. It is decomposed by a current of carbonic acid, with production of pure carbonate of lead; and forms a turbid solution, owing to the formation of a carbonate, when it is mixed with water in which carbonic acid is present. It appears, from the analysis of Berzelius, to consist of one equivalent of acid and three equivalents of the oxide of lead, and is, therefore, a *trisacetate*.

A *diacetate* may likewise be formed by boiling with water a mixture of litharge and acetate of lead in atomic proportion. (Thomson.)

*Acetate of Copper.*—The pigment called *verdigris*, which is an impure acetate of the peroxide of copper, may be formed by exposing metallic copper to the vapour of vinegar, when the metal gradually absorbs oxygen from the atmosphere, and then unites with the acid. It is prepared in large quantity in the south of France by covering copper plates with the refuse of the grape, after the juice has been extracted for making wine. The saccharine matter contained in the husks furnishes acetic acid by fermentation, and in four or six weeks the plates acquire a coating of the acetate.

Verdigris is commonly of a pale green, but sometimes of a blue colour. Its essential constituent is an acetate of copper, composed, according to Mr Phillips*, of 80 parts or one equivalent of the peroxide of copper, 50 parts or one equivalent of acetic acid, and six equivalents of water. This compound is decomposed by water, and is converted into an insoluble green *diacetate*, and into a soluble *binacetate* of copper. The first, as its name implies, consists of one equivalent of acid and two equivalents of the oxide. The binacetate crystallizes readily in rhombic octahedrons of a green colour, and is soluble in twenty times its weight of cold, and five of boiling water It is conveniently prepared by dissolving verdigris in distilled vinegar, and evaporating the solution. The crystals consist of two equivalents of acid and one equivalent of the peroxide of copper, combined, accord-

* Annals of Philosophy, N.S. vol. i. ii. and iv.

ing to Mr Phillips, with three, and, according to Berzelius and Dr Ure, with two equivalents of water.

Besides these compounds, Berzelius has described three other acetates of copper; but as they are of little importance, I refer the reader to the original paper on the subject. (Annals of Philosophy, N. S. vol. viii.)

*Acetate of Zinc.*—This salt may be prepared by way of double decomposition, by mixing sulphate of zinc with acetate of lead in equivalent proportions. When made in this way, it is very apt to retain some sulphate of lead in solution. The best mode of obtaining it quite pure, is by suspending metallic zinc in a dilute solution of the acetate of lead, until all the lead is removed. (Page 354.) This is known to be accomplished by the addition of sulphuretted hydrogen, which then occasions a pure white precipitate. This salt is frequently employed as an astringent collyrium.

*Acetate of Mercury.*—The only interesting compound of mercury and acetic acid is the acetate of the protoxide, which is sometimes employed in the practice of medicine. It is prepared by mixing crystallized protonitrate of mercury with neutral acetate of potassa in the ratio of one equivalent of each. (See the table of atomic weights.) If both salts are dissolved in a considerable quantity of hot water, the solutions retain their transparency after being mixed; but on cooling, the protacetate of mercury is deposited in white scales of a silky lustre. It is easily decomposed; and it should be dried by a very gentle heat, and washed with cold water slightly acidulated with acetic acid.

## *Oxalic Acid.*

Oxalic acid exists ready formed in several plants, especially in the *rumex acetosa* or common sorrel, and in the *oxalis acetosella* or wood sorrel; but it almost always occurs in combination either with lime or potassa. These plants contain the binoxalate of potassa; and the oxalate of lime has been found in large quantity by M. Braconnot in several species of lichen.

Oxalic acid is easily made artificially by digesting sugar in five or six times its weight of nitric acid, and expelling the excess of that acid by distillation, until a fluid of the consistence of syrup remains in the retort. The residue in cooling yields crystals of oxalic acid, the weight of which amounts to rather more than half the quantity of the sugar employed. They should be purified by solution in pure water, and recrystallization. In this process, changes of a very complicated nature ensue, during which a portion of nitric acid is resolved, chiefly into oxygen and deutoxide of nitrogen, while the sugar is converted, with formation of carbonic acid and water, into oxalic acid. A small quantity of malic and acetic acids are generated at the same time. As oxalic acid does not contain any hydrogen, and has a smaller proportional quantity of carbon than sugar, there can be no doubt that the production of this acid essentially depends upon the sugar being deprived of all its hydrogen and a portion of its carbon, by oxygen derived from the nitric acid.

Many organic substances besides sugar, such as starch, gum, most of the vegetable acids, wool, hair, and silk, are converted into oxalic by the action of nitric acid;—a circumstance which is explicable on the fact, that oxalic acid contains more oxygen than any other principle, whether of animal or vegetable origin.

Oxalic acid crystallizes in slender, flattened, four and six-sided prisms, terminated by two-sided summits; but their primary form is an oblique rhombic prism. It has an exceedingly sour taste, reddens litmus paper strongly, and forms neutral salts with alkalies. The crystals effloresce on exposure to the air, but undergo no other change. They are soluble in twice their weight of cold and in their own weight of boiling water. They are dissolved also by alcohol, though less freely than in water. They contain half their weight of water of crystallization, part of which only, amounting to about 28 per cent, can be expelled by heat without decomposing the acid itself.

The atomic weight of oxalic acid, as determined by Dr Thomson, is precisely 36; and the crystals consist of 36 parts or one equivalent of real acid, and 36 parts or four equivalents of water. (First Principles, vol. ii*.) It differs in composition from all other vegetable acids in containing no hydrogen, the absence of which seems fully established by the analyses of Berzelius, Thomson, and Ure. From the researches of these chemists, oxalic acid is composed of one part of carbon and two parts of oxygen; but since its equivalent is 36, it must be regarded as a compound of

| | | | |
|---|---|---|---|
| Carbon | . | 12 | or two equivalents. |
| Oxygen | . | 24 | or three equivalents. |
| | | 36 | |

It is, therefore, intermediate between carbonic oxide and carbonic acid, and may even be supposed to consist of

| | | | |
|---|---|---|---|
| Carbonic oxide | . | 14 | or one equivalent. |
| Carbonic acid | . | 22 | or one equivalent. |
| | | 36 | |

Consistently with this view, Dŏbereiner found that oxalic acid is converted into carbonic acid and carbonic oxide by the action of a very large excess of fuming sulphuric acid. (An. de Ch. et de Ph. vol. xix.) The experiment succeeds even with the common oil of vitriol of commerce.

Oxalic acid is one of the most powerful and rapidly fatal poisons which we possess; and frequent accidents have occurred from its being sold and taken by mistake for Epsom salts, with the appearance of which its crystals have some resemblance. These substances may be easily distinguished, however, by the strong acidity of oxalic acid, which may be tasted without danger, while the sulphate of magnesia is quite neutral and has a bitter saline taste. The experiments of Drs Christison and Coindet have demonstrated that chalk and magnesia are certain antidotes to poisoning by oxalic acid, in consequence of forming with it insoluble and inert compounds. (Edinburgh Medical and Surgical Journal for 1823.)

Oxalic acid is easily distinguished from all other acids by the form of its crystals, and by its solution giving with lime-water a white precipitate, which is insoluble in an excess of the acid.

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* I have reason to believe the composition of crystallized oxalic acid, as stated in the text on the authority of Dr Thomson, to be inexact. Dr Prout assures me of his conviction, arising from repeated experiment, that the crystals consist of 36 parts or one equivalent of real acid, and only 27 parts or three equivalents of water. This proportion coincides with that observed by Berzelius, who found the crystals of oxalic acid to contain rather more than 42 per cent of water

The salts of oxalic acid are termed *oxalates*. Most of these compounds are either insoluble or sparingly soluble in water; but they are all dissolved by the nitric, and also by muriatic acid, except when the latter precipitates the bases of the salts. The only oxalates which are remarkable for solubility are those of potassa, soda, lithia, ammonia, alumina, and iron.

A soluble oxalate is easily detected by adding to its solution a neutral salt of lime or lead, when a white oxalate of those bases will be thrown down. On digesting the precipitate in a little sulphuric acid, an insoluble sulphate is formed, and the solution yields crystals of oxalic acid on cooling. All insoluble oxalates, the bases of which form insoluble compounds with sulphuric acid, may be decomposed in a similar manner. All other insoluble oxalates may be decomposed by potassa, by which means a soluble oxalate is procured.

The oxalates, like all salts which contain a vegetable acid, are decomposed by a red heat, a carbonate being left, provided the oxide can retain carbonic acid at the temperature which is employed. As oxalic acid is so highly oxidized, its salts leave no charcoal when heated in close vessels.

Several oxalates are reduced to the metallic state, with evolution of pure carbonic acid, when heated to redness in close vessels. (Pages 344 and 345.) The peculiar constitution of oxalic acid accounts fo this change; for one equivalent of the acid, to be converted into carbonic acid, requires precisely one equivalent of oxygen, which is the exact quantity contained in the oxide of a neutral protoxalate.

*Oxalates of Potassa.*—Oxalic acid forms with potassa three compounds, of which the description was given, and the composition determined, in the year 1808, by Dr Wollaston. (Philos. Trans. for 1808.) The first is the neutral oxalate which is formed by neutralizing carbonate of potassa with oxalic acid. It crystallizes in oblique quadrangular prisms, which have a cooling bitter taste, require about twice their weight of water at 60° F. for solution, and contain 36 parts or one equivalent of oxalic acid, 48 parts or one equivalent of potassa, and one equivalent of water. This salt is much employed as a reagent for detecting lime. The binoxalate of potassa is contained in sorrel, and may be procured from that plant by solution and crystallization. It crystallizes readily in small rhomboids, which are less soluble in water than the neutral oxalate. It is often sold under the name of *essential salt of lemons* for removing iron moulds from linen;—an effect which it produces by one equivalent of its acid uniting with the oxide of iron and forming a soluble oxalate. The third salt contains twice as much acid as the preceding compound, and has hence received the name of *quadroxalate* of potassa. It is the least soluble of these salts, and is formed by digesting the binoxalate in nitric acid, by which it is deprived of one-half of its base. It is composed of four equivalents of acid, one of potassa, and seven of water.

*Oxalate of Soda,* which may be made in the same manner as oxalate of potassa, is very rarely employed, and is of little importance. It likewise forms a binoxalate, but no quadroxalate is known.

Oxalate of ammonia, prepared by neutralizing that alkali with oxalic acid, is much used as a reagent. It is very soluble in hot water, and is deposited in acicular crystals when a saturated hot solution is allowed to cool. The crystals contain two equivalents of water. Dr Thomson has likewise described a binoxalate of ammonia, which is less soluble than the preceding and contains three equivalents of water.

*Oxalate of Lime.*—This salt, like all the insoluble oxalates, is easily

prepared by the way of double decomposition. It is a white finely divided powder, which is remarkable for its extreme insolubility in pure water. On this account a soluble oxalate is an exceedingly delicate test for lime. It is very soluble, however, in muriatic and nitric acids. It is composed of 36 parts or one equivalent of the acid, and 28 parts or one equivalent of lime. It may be exposed to a temperature of 560° F. without decomposition, and is then quite anhydrous. No binoxalate of lime is known.

This salt is interesting in a pathological point of view, because it is a frequent ingredient of urinary concretions. It is the basis of what is called the *mulberry calculus*.

*Oxalate of Magnesia.*—This salt may be prepared by mixing oxalate of ammonia with a hot concentrated solution of sulphate of magnesia. It is a white powder, which is very sparingly soluble in water; but, nevertheless, when the sulphate of magnesia is moderately diluted with cold water, the oxalate of ammonia occasions no precipitate. On this fact is founded the best analytic process for separating lime from magnesia.

## *Tartaric Acid.*

This acid exists in the juice of several acidulous fruits, but it is almost always in combination with lime or potassa. It is prepared by mixing intimately 198 parts or one equivalent of cream of tartar, in fine powder, with 50 parts or one equivalent of chalk, and throwing the mixture by small portions at a time into ten times its weight of boiling water. On each addition brisk effervescence ensues, owing to the escape of carbonic acid; and one equivalent of the insoluble tartrate of lime subsides, while one equivalent of neutral tartrate of potassa is held in solution. On washing the former with water, and then digesting it, diffused through a moderate portion of water, with one equivalent of sulphuric acid, the tartaric acid is set free; and after being separated from the sulphate of lime by a filter, may be procured by evaporation in prismatic crystals, the primary form of which is a right rhombic prism.

Tartaric acid has a sour taste, which is very agreeable when diluted with water. It reddens litmus paper strongly and forms with alkalies neutral salts, to which the name of *tartrates* is applied. It requires five or six times its weight of water at 60° for solution, and is much more soluble in boiling water. It is dissolved likewise, though less freely, in alcohol. The aqueous solution is gradually decomposed by keeping, and a similar change is experienced under the same circumstances by most of the tartrates. The crystals may be exposed to the air without change. They are converted into the oxalic by digestion in nitric acid. When heated in close vessels, it fuses, froths up, and is decomposed, yielding, in addition to the usual products of destructive distillation, a distinct acid to which the name of *pyrotartaric acid* is applied. A considerable quantity of charcoal remains.

The atomic weight of tartaric acid, inferred by Dr Thomson from the tartrates of potassa and lead, is 66; and the crystals, which cannot be deprived of their water by heat without decomposition, consist of 66 parts or one equivalent of acid, and one equivalent of water. According to the analysis of Dr Prout and Dr Thomson, which agrees pretty closely with that of Berzelius, the acid itself is composed of

| | | | |
|---|---|---|---|
| Carbon | . | 24 | or four equivalents. |
| Oxygen | . | 40 | or five equivalents. |
| Hydrogen | . | 2 | or two equivalents. |
| | | 66 | |

Tartaric acid is distinguished from other acids by forming a white precipitate, the bitartrate of potassa, when mixed with any of the salts of that alkali. This acid, therefore, separates potassa from every other acid. It occasions a white precipitate with lime-water which is very soluble in an excess of the acid.

Tartaric acid is remarkable for its tendency to form double salts, the properties of which are often more interesting than the simple salts. The most important of these double salts, and the only ones which have been much studied, are the tartrate of potassa and soda, and the tartrate of antimony and potassa. The neutral tartrates of the alkalies, of magnesia, and copper, are soluble in water; but most of the tartrates of the other bases, and especially those of lime, baryta, strontia, and lead, are insoluble. All these neutral tartrates, however, which are insoluble in pure water, are soluble in an excess of their acid. They are decomposed by digestion in carbonate of potassa, and when an acid is added in excess, the bitartrate of potassa is precipitated. All the insoluble tartrates are easily procured from the neutral tartrate of potassa by way of double decomposition.

*Tartrates of Potassa.*—The neutral tartrate, frequently called *soluble tartar*, is formed by neutralizing a solution of the bitartrate with carbonate of potassa; and it is a product of the operation above described for making tartaric acid. Its primary form is a right rhomboidal prism; but it often occurs in irregular six-sided prisms with dihedral summits. Its crystals are very soluble in water, and attract moisture when exposed to the air. They consist of 114 parts or one equivalent of the neutral tartrate, and two of water. They are rendered quite anhydrous by a temperature not exceeding 248° Fahr.

Of the *bitartrate*, an impure form, commonly known by the name of *tartar*, is found encrusted on the sides and bottom of wine casks, a source from which all the tartar of commerce is derived. This salt exists in the juice of the grape, and, owing to its insolubility in alcohol, is gradually deposited during the vinous fermentation. In its crude state, it is coloured by the wine from which it was procured; but when purified, it is quite white, and in this state constitutes the *cream of tartar* of the shops.

The bitartrate of potassa is very sparingly soluble in water, requiring sixty parts of cold and fourteen of boiling water for solution, and is deposited from the latter on cooling in small crystalline grains. Its crystals are commonly irregular six-sided prisms, terminated at each extremity by six surfaces; and its primary form is either a right rectangular, or a right rhombic prism. It has a sour taste, and distinct acid reaction. It consists of one equivalent of potassa, and two of the acid, united according to Berzelius with one, and according to Dr Thomson with two equivalents of water. Assuming the latter to be correct, the atomic weight of the bitartrate is 198. Its water of crystallization cannot be expelled without decomposing the salt itself.

The bitartrate of potassa is employed in the formation of tartaric acid and all the tartrates. It is likewise used in preparing pure carbonate of potassa. When exposed to a strong heat, it yields an acrid empyreumatic oil, some pyrotartaric acid, together with water, carburetted hydrogen, carbonic oxide, and carbonic acid gases, the last of which

combines with the potassa. The fixed products are carbonate of potassa and charcoal, which may be separated from each other by solution and filtration. When deflagrated with half its weight of nitre, by which part of the charcoal is consumed, it forms *black flux;* and when an equal weight of nitre is used, so as to oxidize all the free carbon of the tartaric acid, a pure carbonate of potassa, called *white flux*, is procured.

*Tartrate of Potassa and Soda.*—This double salt, which has been long employed in medicine under the name of *Seignette* or *Rochelle salt*, is prepared by neutralizing bitartrate of potassa with carbonate of soda. By evaporation it yields prismatic crystals, the sides of which often amount to ten or twelve in number; but the primary form, as obtained by cleavage, is a right rhombic prism. (Mr Brooke.) The crystals are soluble in five parts of cold and in a less quantity of boiling water, and are composed of 114 parts or one equivalent of tartrate of potassa, 98 parts or one equivalent of tartrate of soda, and eight equivalents of water.

*Tartrate of Soda* is of little importance. It is frequently made extemporaneously by dissolving equal weights of tartaric acid and bicarbonate of soda in separate portions of water, and then mixing the solutions. A very agreeable effervescing draught is procured in this way. Soda is better adapted for this purpose than potassa, because the former has little or no tendency to form an insoluble bitartrate.

*Tartrate of Antimony and Potassa.*—This compound, long celebrated as a medicinal preparation under the name of *tartar emetic*, is made by boiling protoxide of antimony with a solution of bitartrate of potassa. The oxide of antimony is furnished for this purpose in various ways. Sometimes the *glass* or *crocus* of that metal is employed. The Edinburgh college prepare an oxide by deflagrating sulphuret of antimony with an equal weight of nitre; and the college of Dublin employ the submuriate. Mr Phillips recommends that 100 parts of metallic antimony in fine powder should be boiled to dryness in an iron vessel, with 200 parts of sulphuric acid; and that the residual subsulphate be boiled with an equal weight of cream of tartar. The solution of the double salt, however made, should be concentrated by evaporation, and allowed to cool in order that crystals may form.

The tartrate of antimony and potassa commonly crystallizes in tetrahedrons, which are often transparent when first formed, but become white and opake by exposure to the air. It has a styptic metallic taste, reddens litmus paper slightly, and is soluble in fifteen parts of water at 60°, and in three of boiling water. (Dr Duncan, jun.) Its aqueous solution, like that of all the tartrates, undergoes spontaneous decomposition by keeping; and, therefore, if kept in the liquid form, alcohol should be added in order to preserve it. According to the analysis of Dr Thomson, (First Principles, vol. ii. p. 441) it is composed of

| | | | |
|---|---|---|---|
| Tartaric acid | $(66\times2)$ | 132 | or two equivalents. |
| Protoxide of Antimony | $(52\times3)$ | 156 | or three equivalents. |
| Potassa | | 48 | or one equivalent. |
| Water | | 18 | or two equivalents. |
| | | 354 | |

With this result, the analysis of Mr Phillips accords, except that he found three instead of two equivalents of water. The atomic weight of the salt would, on this estimate, be 363.

Tartar emetic is decomposed by many reagents. Thus alkaline substances, from their superior attraction for tartaric acid, separate the

oxide of antimony. The pure alkalies, indeed, and especially potassa and soda, precipitate it imperfectly, owing to their tendency to unite with and dissolve the oxide; but the alkaline carbonates throw down the oxide much more completely. Lime-water occasions a white precipitate, which is a mixture of the oxide or tartrate of antimony, and tartrate of lime. The stronger acids, such as the sulphuric, nitric, and muriatic, cause a white precipitate, consisting of bitartrate of potassa and a sub-salt of antimony. Decomposition is likewise effected by several metallic salts, the bases of which yield insoluble compounds with tartaric acid. Sulphuretted hydrogen throws down the orange sulphuret of antimony. It is precipitated by many vegetable substances, especially by an infusion of gall-nuts, and other similar astringent solutions, with which it forms a dirty white precipitate, which is regarded as a compound of tannin and oxide of antimony. This combination is inert, and therefore a decoction of cinchona bark is recommended as an antidote to tartar emetic.

## *Citric Acid.*

This acid is contained in many of the acidulous fruits, but exists in large quantity in the juice of the lime and lemon, from which it is procured by a process very similar to that described for preparing tartaric acid. To any quantity of lime or lemon juice, finely powdered chalk is added as long as effervescence ensues, and the insoluble citrate of lime, after being well washed with water, is decomposed by digestion in dilute sulphuric acid. The insoluble sulphate of lime is separated by a filter, and the citric acid obtained in crystals by evaporation. They are rendered quite pure by being dissolved in water and re-crystallized. The proportions required in this process are 86 parts or one equivalent of dry citrate of lime, and 49 parts or one equivalent of strong sulphuric acid, which should be diluted with about ten parts of water.

Citric acid crystallizes in rhomboidal prisms terminated by four plane surfaces. The crystals are large and transparent, undergo no change in the air, and if kept dry may be preserved for any length of time without decomposition. They have an intensely sour taste, redden litmus paper, and neutralize alkalies. Their flavour when diluted is very agreeable. They are soluble in an equal weight of cold and in half their weight of boiling water, and are also dissolved by alcohol. The aqueous solution is gradually decomposed by keeping. It is converted into oxalic by the action of nitric acid. Exposed to heat, the crystals undergo the watery fusion, and the acid itself is decomposed before all its water of crystallization is expelled. Besides the usual products of the decomposition of vegetable matter, a peculiar acid sublimes, to which the name of *pyrocitric acid* is applied.

The atomic weight of citric acid, as deduced from the composition of citrate of lead by Thomson and Berzelius, is 58; and the crystals consist of 58 parts or one equivalent of the acid, and 18 parts or two equivalents of water. According to the analyses of the same chemists, this acid is inferred to consist of

| | | | |
|---|---|---|---|
| Carbon | . | 24 | or four equivalents. |
| Oxygen | . | 32 | or four equivalents. |
| Hydrogen | . | 2 | or two equivalents. |
| | | 58 | |

The analysis of Gay-Lussac and Thenard, of Dr Prout and Dr Ure*, would lead to a different statement; but the foregoing agrees better with the atomic weight of the acid.

Citric acid is characterized by its flavour, by the form of its crystals, and by forming an insoluble salt with lime, and a deliquescent soluble compound with potassa. It does not render lime-water turbid, unless the latter is in excess, and fully saturated with lime in the cold.

Critic acid is chiefly employed as a substitute for lemon juice. On some occasions, as in making effervescing draughts or acidulous drinks, tartaric acid may be used with equal advantage.

The salts of citric acid are of little importance. The citrates of potassa, soda, ammonia, magnesia, and iron, are soluble in water. The first is often made extemporaneously as an effervescing draught. The citrates of lime, baryta, and strontia, lead, mercury, and silver, are very sparingly soluble. All of them are dissolved by an excess of their own acid, and are decomposed by sulphuric acid.

## *Malic Acid.*

This acid is contained in most of the acidulous fruits, being frequently associated with the tartaric and citric acids. Grapes, currants, gooseberries, and oranges contain it. Vauquelin found it in the tamarind, mixed with tartaric and citric acids, and in the house leek, (*sempervivum tectorum,*) combined with lime. It is contained in considerable quantity in apples, a circumstance to which it owes its name. It is almost the sole acidifying principle of the berries of the service tree (*sorbus aucuparia,*) in which it was detected by Mr Donovan, and described by him under the name of *sorbic acid* in the Philosophical Transactions for 1815; but it was afterwards identified with the malic acid by Braconnot and Houton-Labillardière. (An. de Ch. et de Ph. vol. viii.)

Malic acid may be formed by digesting sugar with three times its weight of nitric acid; but the best mode of procuring it is from the berries of the service tree. The juice of the unripe berries is diluted with three or four parts of water, filtered, and heated; and while boiling, a solution of acetate of lead is added as long as any turbidity appears. The colouring matter of the berry is thus precipitated, while malate of lead remains in solution. The liquid, while at a boiling temperature, is then filtered. At first a small quantity of dark coloured salt subsides; but on decanting the hot solution into another vessel, the malate of lead is gradually deposited, in cooling, in groups of brilliant white crystals. This process—a modification of the common one—has lately been recommended by Wöhler. The malate of lead is then decomposed by a quantity of dilute sulphuric acid, insufficient for combining with all the oxide of lead; by which means a solution is procured containing malic acid together with a little lead. The latter is afterwards precipitated by sulphuretted hydrogen.

Malic acid has a very pleasant acid taste. It crystallizes with great difficulty and in an imperfect manner, attracts moisture from the atmosphere, and is very soluble in water and alcohol. Its aqueous solution is gradually decomposed by keeping. Nitric acid converts it into oxalic acid. Heated in close vessels, it is decomposed with formation of a new and volatile acid, which has hence received the name of *pyromalic acid.*

* Philosophical Transactions for 1812.

According to a recent analysis of the malates of lime, lead, and copper by Dr Prout, 100 parts of anhydrous malic acid consist of 40.68 parts of carbon, 54.24 of oxygen, and 5.08 parts of hydrogen.

Most of the salts of malic acid are more or less soluble in water. The malates of soda and potassa are deliquescent and very soluble. Those of lead and lime, the most insoluble of the malates, are sparingly soluble in cold water, but are freely dissolved by that liquid at a boiling temperature, a circumstance which distinguishes the malic from the oxalic, tartaric, and citric acids.

## *Benzoic Acid.*

Benzoic acid exists in gum benzoin, in storax, in the balsams of Peru and Tolu, and in several other vegetable substances. M. Vogel has detected it in the flowers of the *trifolium melilotus officinalis.* It is found in considerable quantity in the urine of the cow and other herbivorous animals, and is perhaps derived from the grasses on which they feed. It has also been detected in the urine of children.

This acid is commonly extracted from gum benzoin. One method consists in heating the benzoin in an earthen pot, over which is placed a cone of paper to receive the acid as it sublimes; but since the product is always impure, owing to the presence of empyreumatic oil, it is better to extract the acid by means of an alkali. The usual process consists in boiling finely powdered gum benzoin in a large quantity of water along with lime or carbonate of potassa, by which means a benzoate is formed. To the solution, after being filtered and concentrated by evaporation, muriatic acid is added, which unites with the base, and throws down the benzoic acid. It is then dried by a gentle heat, and purified by sublimation.

Benzoic acid has a sweet and aromatic rather than a sour taste; but it reddens litmus paper, and neutralizes alkalies. It fuses readily by heat, and at a temperature a little above its point of fusion, it is converted into vapour, emitting a peculiar, fragrant, and highly characteristic odour, and condensing on cool surfaces without change. When strongly heated, it takes fire, and burns with a clear yellow flame. It undergoes no change by exposure to the air, and is not decomposed by the action even of nitric acid. It requires about 24 parts of boiling water for solution, and nearly the whole of it is deposited on cooling in the form of minute acicular crystals of a silky lustre. It is very soluble in alcohol, especially by the aid of heat.

Benzoic acid is easily distinguished by its odour and volatility. Its salts are all decomposed by muriatic acid, with deposition of benzoic acid, if the solution is moderately concentrated.

The atomic weight of benzoic acid, as inferred from the analysis of benzoate of lead by Berzelius, and that of the benzoate of the peroxide of iron by Dr Thomson, is 120.

The ultimate analysis of this acid by Berzelius*, together with the number representing the weight of its combining proportion, appears to justify the opinion that it is composed of

| | | |
|---|---|---|
| Carbon . . | 90 | or fifteen equivalents. |
| Oxygen . . | 24 | or three equivalents. |
| Hydrogen . . | 6 | or six equivalents. |
| | 120 | |

* Annals of Philosophy, vol. v.

According to the analysis of Dr Ure, it contains thirteen instead of fifteen equivalents of carbon. (Philos. Trans. for 1822.)

Most of the benzoates are soluble in water. Those of lead, mercury, and peroxide of iron are the most insoluble. The benzoates of soda and ammonia are sometimes employed for separating iron from manganese. If the solution is quite neutral, the peroxide of iron is completely precipitated, while the manganese remains in solution.

## Gallic Acid.

This acid was discovered by Scheele in 1786, and exists ready formed in the bark of many trees, and in gall-nuts. It is always associated with tannin, a substance to which it is allied in a manner hitherto unexplained.

Several processes have been described for the preparation of gallic acid; but the most economical appears to be that of Scheele, as modified by M. Braconnot. (An. de Ch. et de Ph. vol. ix.) Any quantity of gall-nuts, reduced to powder, is infused for a few days in four times their weight of water; and the infusion, after being strained through linen, is kept for two months in a moderately warm atmosphere. During this period, the surface of the liquid becomes mouldy, the tannin of the gall-nuts disappears more or less completely, and a yellowish crystalline matter is deposited. On evaporating the solution to the consistence of syrup, and allowing it to cool, an additional quantity of the same substance subsides. The gallic acid, thus procured. is impure, owing to the presence of colouring matter, and a peculiar acid, to which M. Braconnot has applied the name of *ellagic acid*. The gallic acid is separated from the latter by boiling water, in which the ellagic acid is insoluble; and it is rendered white by digestion with animal charcoal, deprived of its phosphate of lime by muriatic acid. When the colourless solution is concentrated by evaporation, the gallic acid is deposited in small white acicular crystals of a silky lustre. Some crystals prepared by Mr Phillips, and examined by Mr Brooke, were in the form of an oblique rhombic prism.

Gallic acid has a weak sour taste, accompanied with a slight sensation of astringency. It reddens litmus paper, and effervesces with alkaline carbonates. It is soluble in twenty-four parts of cold and in three of boiling water; and it is likewise dissolved by alcohol. The aqueous solution becomes mouldy by keeping. Nitric acid converts it into oxalic acid. When strongly heated in the open air, it takes fire. At a high temperature in close vessels, it is in part decomposed, and in part sublimes, apparently without change.

The composition and atomic weight of gallic acid has not been determined in a satisfactory manner. From an analysis of the gallate of lead by Berzelius, the equivalent of the acid is probably about 63 or 64; and according to the same chemist it is composed of

| | |
|---|---|
| Carbon | 56.64 |
| Oxygen | 38.36 |
| Hydrogen | 5.00* |

With lime-water, gallic acid yields a brownish-green precipitate, which is redissolved by an excess of the solution, and acquires a reddish tint. It is distinguished from tannin by causing no precipitate in a solution of gelatine. With a salt of iron, it forms a dark blue-coloured compound, which is the basis of ink. The finest colour is procured when the peroxide and protoxide of iron are mixed together. This

* Annals of Philosophy, vol. v.

character distinguishes gallic acid from every other substance excepting tannin.

The salts of gallic acid, called *gallates*, have been imperfectly examined. The gallates of potassa, soda, and ammonia are soluble in water; but most of the other gallates are of sparing solubility. On this account many of the metallic solutions are precipitated by gallic acid.

## *Succinic Acid.*

This acid is procured by heating powdered amber in a retort by a regulated temperature, when the succinic acid passes over and condenses in the receiver. It is at present uncertain whether it exists ready formed in amber, or is a product of the destructive distillation. As first obtained, it has a yellow colour and peculiar odour, owing to the presence of some empyreumatic oil; but it is rendered quite pure and white by being dissolved in nitric acid, and then evaporated to dryness. The oil is decomposed, and the succinic acid left unchanged.

Succinic acid has a sour taste, and reddens litmus paper. It is soluble both in water and alcohol, and crystallizes by evaporation in anhydrous prisms. When briskly heated, it fuses, undergoes decomposition, and in part sublimes, emitting a peculiar and very characteristic odour.

The salts of succinic acid have been little examined. The succinates of the alkalies are soluble in water. That of ammonia is frequently employed for separating iron from manganese, the succinate of the peroxide of iron being quite insoluble in water, provided the solutions are neutral. The succinate of manganese, on the contrary, is soluble.

The atomic weight of succinic acid, deduced from the composition of the succinate of iron and of lead by Thomson and Berzelius, is 50; and, according to the analysis of the succinate of lead by Berzelius, this acid is inferred to consist of

| | | |
|---|---|---|
| Carbon . . | 24 | or four equivalents. |
| Oxygen . . | 24 | or three equivalents. |
| Hydrogen . . | 2 | or two equivalents. |
| | 50 | |

From this it appears that the succinic is identical with the acetic acid, both in the proportion of its constituents and the number of its equivalent. If this is true, and there seems no good reason to doubt the accuracy of the data, the sole difference between these acids consists in the manner in which their elements are combined, a circumstance which is very favourable to the opinion already mentioned relative to the constitution of organic substances in general. (Page 422.)*

*Camphoric Acid.*—This compound has not hitherto been found in any plant, and is procured only by digesting camphor for a considerable time in a large excess of nitric acid. It is sparingly soluble in water. Its taste is rather bitter, and its odour somewhat similar to saffron. It reddens litmus paper, and combines with alkalies, forming salts which are called *camphorates*. This acid has not been applied to any useful purpose.

* If, however, the analysis of acetic acid by Dr Prout be assumed as correct, this identity of composition between it and succinic acid will disappear. (See page 427.) B.

The *mucic* or *saccholactic acid* was discovered by Scheele in 1780. It is obtained by the action of nitric acid on certain substances, such as gum, manna, and the sugar of milk. The readiest and cheapest mode of forming it, is by digesting gum with three times its weight of nitric acid. On applying heat, effervescence ensues, and three acids—the oxalic, malic, and saccholactic, are the products. The latter, from its insolubility, subsides as a white powder, and may be separated from the others by washing with cold water. In this state Dr Prout says it is very impure. To purify it he digests with a slight excess of ammonia, and dissolves the resulting salts in boiling water. It is filtered while hot, and the solution evaporated slowly almost to dryness. The saccholactate of ammonia is thus obtained in crystals, which are to be washed with cold distilled water, until they become quite white. They are then dissolved in boiling water, and the saturated hot solution dropped into cold dilute nitric acid.

The saccholactic is a weak acid, which is insoluble in alcohol, and requires sixty times its weight of boiling water for solution. When heated in a retort it is decomposed, and in addition to the usual products, yields a volatile white substance, to which the name of *pyromucic acid* has been applied. According to the analysis of Dr Prout, saccholactic acid is composed of 33 parts of carbon, 61.5 of oxygen, and 4.9 of hydrogen.

*Moroxylic Acid.*—This compound, which was discovered by Klaproth, is found in combination with lime on the bark of the *morus alba* or white mulberry, and has since received the appellation of *moric* or *moroxylic acid*. It is obtained by decomposing the moroxylate of lime by acetate of lead, and then separating the lead from the moroxylate of that base by means of sulphuric acid.

The *hydrocyanic* or *prussic acid*, which is not an unfrequent production of plants, has already been described.

The *sorbic*, as already mentioned, has been shown to be the malic acid.

*Rheumic Acid.*—This name was applied to the acid principle contained in the stem of the garden rhubarb; but M. Lassaigne has shown it to be the oxalic acid.

*Boletic acid* was discovered by M. Braconnot, in the juice of the *Boletus pseudo-igniarius*. As it is a compound of no importance, I refer the reader to the original paper for an account of it. (Annals of Phil. vol. ii.)

*Igasuric Acid.*—MM. Pelletier and Caventou have proposed this name for the acid which occurs in combination with strychnia in the nux vomica and St Ignatius's bean; but its existence, as different from all other known acids, is doubtful.

*Mellitic Acid.*—This acid is contained in the rare substance called *honey-stone*, which is occasionally met with at Thuringia in Germany. The honey-stone, according to Klaproth, is a mellitate of alumina, and on boiling it in a large quantity of water, the acid is dissolved and the alumina subsides. On concentrating the solution, the mellitic acid is deposited in minute acicular crystals. From its rarity it has been little studied, and is of little importance.

*Suberic acid* is procured by the action of nitric acid on cork. Its acid properties are feeble. It is very soluble in boiling water, and the greater part of it is deposited from the solution in cooling in the form of a white powder. Its salts, which have been little examined, are known by the name of *suberates*.

*Zumic Acid.*—This compound, procured by Braconnot from several vegetable substances which had undergone the acetous fermenta-

tion, appears from the observations of Vogel to be the lactic acid. (Annals of Philosophy, vol. xii.)

*Kinic Acid.*—This acid exists in the cinchona bark in combination with lime. On evaporating an infusion of bark to the consistence of an extract, and treating the residue with alcohol, a viscid matter remains, consisting of the kinate of lime and mucilaginous matters. On dissolving it in water, and allowing the concentrated solution to evaporate spontaneously in a warm place, the kinate crystallizes in rhombic prisms with dihedral summits. From a solution of this salt, Vauquelin precipitated the lime by means of oxalic acid, and thus obtained kinic acid in a pure state. (An. de Ch. vol. lix.)

Kinic acid has an acid taste and reddens vegetable blue colours. It is very soluble in water, and crystallizes with difficulty. It forms soluble compounds with the alkalies and alkaline earths, and is not precipitated by a salt of mercury, lead, or silver.

*Meconic acid*, which is combined with morphia in opium, will be most conveniently described in the following section.

*Pectic Acid.*—See Vegetable Jelly.

*Carbazotic Acid.*—This name has been applied by M. Liebig to a peculiar acid, formed by the action of nitric acid on indigo. It is made by dissolving small fragments of the best indigo in eight or ten times their weight of moderately strong nitric acid, and boiling the solution as long as nitrous acid fumes are evolved. On cooling, a large quantity of semi-transparent yellow crystals will be formed ; and on evaporating the residual liquid, and adding cold water, an additional quantity of the acid is procured. To render the new acid quite pure it should be dissolved in hot water, and neutralized by carbonate of potassa. As the liquid cools, the carbazotate of potassa crystallizes, and may be purified by repeated crystallization. The acid may be precipitated from this salt by sulphuric acid.

Carbazotic acid is sparingly soluble in cold water ; but is dissolved much more freely by the aid of heat, and on cooling yields brilliant crystalline plates of a yellow colour. Ether and alcohol dissolve it readily. It is fused and volatilized by heat without decomposition; but when suddenly exposed to a strong heat, it inflames without explosion, and burns with a yellow flame, with a residue of charcoal. Its solution has a bright yellow colour, reddens litmus paper, is extremely bitter, acts like a strong acid on metallic oxides, and yields crystallizable salts. It is composed of carbon, nitrogen, and oxygen, in the proportion of fifteen equivalents of the first, three of the second, and fifteen of the third substance. (Journal of Science, vols. ii. 210, and iii. 490.)

The bitter principle of Welter, formed by the action of nitric acid on silk, is also carbazotic acid.

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# SECTION II.

## *VEGETABLE ALKALIES.*

Under this title are comprehended those proximate vegetable principles which are possessed of alkaline properties. The honour of discovering the existence of this class of bodies is due to Sertuerner,

a German apothecary, who published an account of morphia so long ago as the year 1803; but the subject excited no notice until the publication of his second essay in 1816. The chemists who have since cultivated this department with most success are M. Robiquet, and MM. Pelletier and Caventou.

All the vegetable alkalies, according to the researches of Pelletier and Dumas, consist of carbon, hydrogen, oxygen, and nitrogen. (An. de Ch. et de Ph. vol. xxiv.) They are decomposed with facility by nitric acid and by heat, and ammonia is always one of the products of the destructive distillation. They never exist in an insulated state in the plants which contain them; but are apparently in every case combined with an acid, with which they form a salt more or less soluble in water. These alkalies are for the most part very insoluble in water, and of sparing solubility in cold alcohol; but they are all readily dissolved by that fluid at a boiling temperature, being deposited from the solution, commonly in the form of crystals, on cooling. Most of the salts are far more soluble in water than the alkalies themselves, and several of them are remarkable for their solubility.

As the vegetable alkalies agree in several of their leading chemical properties, the mode of preparing one of them admits of being applied with slight variation to all. The general outline of the method is as follows.—The substance containing the alkaline principle is digested, or more commonly macerated, in a large quantity of water, which dissolves the salt, the base of which is the vegetable alkali. On adding some more powerful salifiable base, such as potassa or ammonia, or boiling the solution for a few minutes with lime or pure magnesia, the vegetable alkali is separated from its acid, and being in that state insoluble in water, may be collected on a filter and washed. As thus procured, however, it is impure, retaining some of the other principles, such as the oleaginous, resinous, or colouring matters, with which it is associated in the plant. To purify it from these substances, it should be mixed with a little animal charcoal, and dissolved in boiling alcohol. The alcoholic solution, which is to be filtered while hot, yields the pure alkali, either on cooling or by evaporation; and if not quite colourless, it should again be subjected to the action of alcohol and animal charcoal. In order to avoid the necessity of employing a large quantity of alcohol, the following modification of the process may be adopted. The vegetable alkali, after being precipitated and collected on a filter, is made to unite with some acid, such as the acetic, sulphuric, or muriatic, and the solution boiled with animal charcoal, until the colouring matter is removed. The alkali is then precipitated by ammonia or some other salifiable base.

## *Morphia.*

Opium contains a great diversity of different principles, among which the following may in particular be enumerated:—morphia, meconic acid, narcotine, gummy resinous and extractive colouring matters, lignin, fixed oil, and a small quantity of caoutchouc. On infusing opium in water, several of these principles are dissolved, and especially the meconate of morphia, together with narcotine, which is likewise rendered soluble by an acid.

One of the best processes for preparing pure morphia is that recommended by M. Robiquet. (An. de Ch. et de Ph. vol. v.) The concentrated infusion of a pound of opium is boiled for a quarter of an hour with about 150 grains of pure magnesia, and the grayish crystalline precipitate, which consists of the meconate of magnesia, mor-

phia, narcotine, colouring matter, and the excess of magnesia, is collected on a filter and edulcorated with cold water. This powder is then digested at a temperature of 120° or 130° F. in dilute alcohol, which removes the narcotine and the greater part of the colouring matter. The morphia is then taken up by concentrated boiling alcohol, and is deposited in crystals on cooling. Dr Christison informs me that by this process, conducted in the laboratory of M. Robiquet, he procured three drachms and a half of morphia from half a pound of a very pure specimen of the best Turkey opium.

Dr Thomson proposes to precipitate the morphia by ammonia, and to purify it by solution in acetic acid and digestion with animal charcoal. (Annals of Phil. vol. xv.) This process is very convenient, but I doubt if it gives so large a product as the foregoing. The animal charcoal should be deprived of phosphate of lime by muriatic acid before being used.

Pure morphia crystallizes readily when its alcoholic solution is evaporated, and yields colourless crystals of a brilliant lustre. They mostly occur in irregular six-sided prisms with dihedral summits; but their primary form is a right rhombic prism, of which the lateral planes only appear in the crystals. (Brooke.) It is almost wholly insoluble in cold, and to very small extent in hot water. It is soluble in strong alcohol, especially by the aid of heat. In its pure state, it has scarcely any taste; but when rendered soluble by combining with an acid or by solution in alcohol, it is intensely bitter. It has an alkaline reaction, and combines with acids, forming neutral salts, which are far more soluble in water than morphia itself, and for the most part are capable of crystallizing.

Strong nitric acid decomposes morphia, forming a red solution, which by the continued action of the acid acquires a yellow colour, and is ultimately converted into oxalic acid. This circumstance was first noticed by Pelletier and Caventou; but it is not peculiar to morphia, since nitric acid has a similar effect on strychnia.

Morphia is the narcotic principle of opium. When pure, owing to its insolubility, it is almost inert; for M. Orfila gave twelve grains of it to a dog without its being followed by any sensible effect*. In a state of solution, on the contrary, it acts on the animal system with great energy, Sertuerner having noticed alarming symptoms from so small a quantity as half a grain. From this it appears to follow that the effects of an overdose of a salt of morphia may be prevented by giving a dilute solution of ammonia, or an alkaline carbonate, so as to precipitate the vegetable alkali. When carefully administered, morphia may be employed very advantageously in the practice of medicine; since, according to Magendie, it produces the soothing effects of opium, without causing the feverish excitement, heat, and headach, which so frequently accompany the employment of that drug. The best mode of exhibiting it, is in the form of acetate of morphia, a salt which is very soluble in water, and crystallizes in divergent prisms by evaporation. The basis of Battley's sedative liquor is supposed to be

* Judging from my own experience, I cannot believe that Orfila is accurate in asserting that pure morphia is nearly inert: I have myself employed it on several occasions with very marked effects. Even admitting that, as a general rule, insoluble substances have no action on the animal economy, it may be a question whether morphia is not dissolved by the acid which it meets with in the stomach. B.

acetate of morphia. This compound, from being inodorous, and therefore less easily detected than opium, has been employed for criminal purposes, and M. Lassaigne has described the following method for discovering its presence. (An de Ch. et de Ph. xxv. 102.) The suspected solution is evaporated by a temperature of 212°, and the residue treated with alcohol, by which the acetate of morphia, together with osmazome and some salts, is dissolved. The alcohol is next evaporated, and water added to separate some fatty matter. The aqueous solution is then set aside for spontaneous evaporation, during which the acetate of morphia, if present, crystallizes in divergent prisms of a yellowish colour. The salt is recognised by its bitter taste, by yielding a precipitate with ammonia, by the disengagement of acetic acid on the addition of concentrated sulphuric acid, and by the orange-red colour developed by nitric acid.

The composition of morphia, as will appear from the following numbers, has been stated differently by different chemists. The specimen analyzed by Dr Thomson must surely have been impure.

| | *Pelletier and Dumas.* | *Bussy.* | *Brande.* | *Thomson.* |
|---|---|---|---|---|
| Carbon . | 72.02 | 69.0 | 72.0 | 44.72 |
| Oxygen . | 14.84 | 20.0 | 17.0 | 49.69 |
| Hydrogen . | 7.61 | 6.5 | 5.5 | 5.59 |
| Nitrogen . | 5.53 | 4.5 | 5.5 | 0.00 |
| | 100 | 100 | 100 | 100 |

*Meconic Acid.**—This acid was procured by M. Robiquet from the magnesian precipitate above mentioned, after the morphia had been separated from it. The meconate of magnesia is dissolved in dilute sulphuric acid, and muriate of baryta is then added, which throws down the sulphate and meconate of that base. By acting on this precipitate with dilute sulphuric acid, the meconic acid is set free, and crystallizes when its solution is evaporated. As it retains colouring matter very obstinately, it should be purified by sublimation. Meconic acid may easily be prepared, as recommended by Dr Hare, by precipitating the acid from an aqueous infusion of opium with acetate of lead, and decomposing the insoluble meconate of lead, while diffused through water, by a current of sulphuretted hydrogen gas. The filtered solution yields crystals of meconic acid by evaporation.

Meconic acid has a sour, followed by a bitter taste, reddens litmus paper, and is very soluble both in water and alcohol. It is characterized by giving a red colour to a salt of the peroxide of iron, and communicates an emerald green tint to sulphate of copper. It exerts no action on the animal system. Its presence even in a dilute solution of opium may be detected by acetate of lead. The insoluble meconate of lead, which subsides, is decomposed by sulphuric acid; and on adding a persalt of iron, the red colour caused by the free meconic acid makes its appearance.

*Narcotine.*—This substance, though not regarded as a vegetable alkali, may be conveniently noticed in connection with morphia. It was particularly described in 1803 by Derosne, and was long known by the name of *the salt of Derosne*. Sertuerner supposed it to be the meconate of morphia; but M. Robiquet proved that it is an independent principle, and applied to it the name of *narcotine*. It is easily prepared by evaporating an aqueous infusion of opium to the consistence

* Μηκων *papaver.*

of an extract, and digesting it in sulphuric ether. This solvent, which does not act on the meconate of morphia, takes up all the narcotine, and deposites it in acicular crystals by evaporation, and the extract of opium, thus deprived of narcotine, may be advantageously employed in medical practice. Morphia may be purified from narcotine in the same manner.

Pure narcotine is insoluble in cold and very slightly soluble in hot water. It dissolves in oil, ether, and alcohol, the latter, though diluted, acting as a solvent for it by the aid of heat. It does not possess alkaline properties, though it is rendered soluble in water by means of an acid. Its presence in an aqueous solution of opium seems owing to a free acid, which M. Robiquet imagines to be different from the meconic. Like the vegetable alkalies, nitrogen enters into its constitution.

The unpleasant stimulating properties of opium are attributed by Magendie to the presence of narcotine the ill effects of which, according to the experiments of the same physiologist, are in a great degree counteracted by acetic acid. These results, though they require confirmation, render it probable that the superiority assigned to the *black drop* over the common tincture of opium of the Pharmacopœia is owing to the vegetable acids which enter into its composition.

## *Cinchonia and Quinia.*

The existence of a distinct vegetable principle in cinchona bark was inferred by Dr Duncan, junior, in the year 1803, who ascribed to it the febrifuge virtues of the plant, and proposed for it the name of *cinchonin**. Dr Gomez of Lisbon, whose attention was directed to the subject by the researches of Dr Duncan, succeeded in procuring cinchonin in a separate state; but its alkaline nature was first discovered in 1820 by MM. Pelletier and Caventou. It has been fully established by the labours of those chemists that the febrifuge property of bark is possessed by two alkalies, the *cinchonia* or cinchonin of Dr Duncan, and *quinia*, both of which are combined with kinic acid. These principles, though very analogous, are distinctly different, standing in the same relation to each other as potassa and soda. The former exists in the *Cinchona condaminea*, or pale bark; the latter is present in the *C. cordifolia*, or yellow bark; and they are both contained in the *C. oblongifolia*, or red bark. They were procured by Pelletier and Caventou by a process similar to that of M. Robiquet for preparing morphia†; and slight modifications of the method have been proposed by M. Badollier and M. Voreton‡. From one pound of yellow bark, M. Voreton procured 80 grains of quinia, which is nearly 1.4 per cent.

Pure cinchonia is white and crystalline, requires 2500 times its weight of boiling water for solution, and is insoluble in cold water. Its proper menstruum is boiling alcohol; but it is dissolved in small quantity by oils and ether. Its taste is bitter, though slow in being perceived, on account of its insolubility; but when the alkali is dissolved by alcohol or an acid, the bitterness is very powerful, and accompanied by the flavour of cinchona bark. Its alkaline properties are exceedingly well marked, since it neutralizes the strongest acids. The sulphate, muriate, nitrate, and acetate of cinchonia are soluble in

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* Edinburgh New Dispensatory, 11th edit. p. 299, or Nicholson's Journal for 1803.

† Ann. de Ch. et de Ph. vol. xv. ‡ Ibid. vol. xvii.

water, and the sulphate crystallizes in very short six-sided prisms, derived from an oblique rhomboidal prism. It commonly occurs in twin crystals. The neutral tartrate, oxalate, and gallate of cinchonia are insoluble in cold, but may be dissolved by hot water, or by alcohol.

Quinia, which was discovered by Pelletier and Caventou, does not crystallize like cinchonia when precipitated from its solutions, but it has a white, porous, and rather flocculent aspect. It is very soluble in alcohol, forming a solution which is intensely bitter, and possesses a* distinct alkaline reaction. Ether likewise dissolves it, but it is almost insoluble in water. Its febrifuge virtues are more powerful than those of cinchonia, and it is now extensively employed in the practice of medicine. It is most commonly exhibited in the form of the sulphate, a salt of such activity, that three grains have been known to cure an intermittent fever. This salt, which consists of 90 parts of the alkali and 10 of the acid, crystallizes in delicate white needles, having the appearance of amianthus. It is less soluble in water than the sulphate of cinchonia, but is very bitter. It dissolves readily in strong alcohol by the aid of heat, a character which affords a useful test of its purity.

The analyses of different chemists, relative to the composition of cinchonia and quinia, do not correspond better than those of morphia, as appears by the following results:—

| | *Pelletier and Dumas.* | | *Brande.* | |
|---|---|---|---|---|
| | *Cinchonia.* | *Quinia.* | *Cinchonia.* | *Quinia.* |
| Carbon . | 76.97 | 75.02 | 79.30 | 73.80 |
| Oxygen . | 7.79 | 10.43 | 0.00 | 5.55 |
| Hydrogen | 6.22 | 6.66 | 7.17 | 7.65 |
| Nitrogen | 9.02 | 8.45 | 13.72 | 13.00 |
| | 100.00 | 100.56 | 100.19 | 100.00 |

The neutral gallate, tartrate, and oxalate of quinia, like the analogous salts of cinchonia, are insoluble in cold water.

From the new facts which have been ascertained relative to the constituents of bark, the action of chemical tests on a decoction of this substance is now explicable. According to the analysis of Pelletier and Caventou, the different kinds of Peruvian bark, besides the kinate of cinchonia or quinia, contain the following substances:—a greenish fatty matter; a red insoluble matter; a red soluble principle, which is a variety of tannin; a yellow colouring matter; kinate of lime; gum, starch, and lignin. It is hence apparent that a decoction of bark, owing to the tannin which it contains, may precipitate a solution of tartar emetic, of gelatin, or a salt of iron, without containing a trace of the vegetable alkali, and consequently without possessing any febrifuge virtues.

An infusion of gall-nuts, on the contrary, causes a precipitate only by its gallic acid uniting with cinchonia or quinia, and, therefore, affords a test for distinguishing a good from an inert variety of bark.

## *Strychnia.—Brucia.*

*Strychnia.*—Strychnia was discovered in 1818 by Pelletier and Caventou in the fruit of the *Strychnos ignatia* and *Strychnos nux*

* See Ann. de Chim. et de Phys. xxiv. p. 163.

*vomica*, and has since been extracted by the same chemist from the Upas. (An. de Ch. et de Ph. vols. x. and xxvi.)

The most economical process for preparing this alkali is that recommended by M. Corriol. (Journal de Pharmacie for October 1825, p. 492.) It consists in treating *nux vomica* with successive portions of cold water, evaporating this solution to the consistence of syrup, and precipitating the gum, which is present, by alcohol. The alcoholic solution is then evaporated to the consistence of an extract by the heat of a water-bath. The extract, which consist almost entirely of the igasurate of strychnia, is dissolved by cold water, and by this means deprived of a little fatty matter, which had originally been dissolved, probably through the medium of the gum. The solution is next heated, and the strychnia precipitated by a slight excess of lime-water, and then dissolved by boiling alcohol. On evaporating the spirit, the alkali is obtained pure, except in containing a little brucia and colouring matter, both of which are effectually removed by maceration in dilute alcohol.

Strychnia is very soluble in boiling alcohol, and is procured in minute four-sided prisms by allowing the solution to evaporate spontaneously. It is almost insoluble in water, requiring more than 6000 parts of cold and 2500 of boiling water for solution; but notwithstanding its sparing solubility, it excites an insupportable bitterness in the mouth. Water containing only 1-600,000th of its weight of strychnia has a bitter taste. It has a distinct alkaline reaction, and neutralizes acids, forming salts, most of which are soluble in water. It is united in the *nux vomica* and St Ignatius's bean with igasuric acid. (Page 441.) By the action of strong nitric acid, it yields a red colour; but it appears probable, from some recent observations of Pelletier and Caventou, that the red tint is owing to the presence of some impurity.

Strychnia is one of the most virulent poisons hitherto discovered, and is the poisonous principle of the substance in which it is contained. Its energy is so great, that half a grain blown into the throat of a rabbit occasioned death in the course of five minutes. Its operation is always accompanied with symptoms of locked jaw and other tetanic affections.

Strychnia, according to the analysis of Pelletier and Dumas, is composed of 78.22 of carbon, 6.38 of oxygen, 6.54 of hydrogen, and 8.92 of nitrogen.

*Brucia.*—This alkali was discovered in the *Brucea antidysenterica* by Pelletier and Caventou soon after their discovery of strychnia, (An. de Ch. et de Ph. vol. xii.); and it likewise exists in small quantity in the St Ignatius's bean and *nux vomica*. In its bitter taste and poisonous qualities, it is very similar to strychnia, but is twelve or sixteen times less energetic than that alkali. It is soluble both in hot and cold alcohol, especially in the former; and it crystallizes when its solution is evaporated. Even dilute alcohol by aid of heat dissolves it, and on this property is founded the method of separating it from strychnia. It is more soluble in water than most of the other vegetable alkalies, requiring only 850 times its weight of cold, and 500 of boiling water for solution. It is composed of 75.04 of carbon, 11.21 of oxygen, 6.52 of hydrogen, and 7.22 of nitrogen.

## *Veratria, Emetia, Picrotoxia, Solania, Delphia, &c.*

*Veratria.*—The medicinal properties of the seeds of the *Veratrum sabadilla*, and the root of the *Veratrum album* or white hellebore,

and *Colchicum autumnale* or meadow saffron, are owing to the peculiar alkaline principle *veratria*, which was discovered by Pelletier and Caventou in 1819, and may be extracted by the usual process. (Journal de Pharmacie, vol. vi.) This alkali, which appears to exist in those plants in combination with gallic acid, is white and pulverulent, inodorous, and of an acrid taste. It requires 1000 times its weight of boiling, and still more of cold water for solution. It is very soluble in alcohol, and may also be dissolved, though less readily, by means of ether. It has an alkaline reaction, and neutralizes acids; but it is a weaker base than morphia, quinia, or strychnia. It acts with singular energy on the membrane of the nose, exciting violent sneezings though in very minute quantity. When taken internally in very small doses, it produces excessive irritation of the mucous coat of the stomach and intestines; and a few grains were found to be fatal to the lower animals.

Veratria, according to the analysis of Pelletier and Dumas, consists of 66.75 of carbon, 19.6 of oxygen, 8.54 of hydrogen, and 5.04 of nitrogen.

*Emetia.*—Ipecacuanha consists of an oily matter, gum, starch, lignin, and a peculiar principle, which was discovered in 1817 by M. Pelletier, and to which he has applied the name of *emetine*. (Journal de Pharmacie, vol. iii.) This substance, of which ipecacuanha contains 16 per cent, appears to be the sole cause of the emetic properties of that root, and is procured by a process similar to that for preparing the other vegetable alkalies.

Emetia is a white pulverulent substance, of a rather bitter and disagreeable taste, sparingly soluble in cold, but more freely in hot water, and insoluble in ether. It is readily dissolved by alcohol. At 122° it fuses. It has a distinct alkaline reaction, and neutralizes acids; but its salts are little disposed to crystallize. (An. de Ch. et de Ph. vol. xxiv. p. 181.) According to Pelletier and Dumas, it consists of carbon 64.57, oxygen 22.95, hydrogen 7.77, and nitrogen 4.3.

*Picrotoxia.*—The bitter poisonous principle of the *cocculus indicus* was discovered in 1819 by M. Boullay, who gave it the name of *picrotoxine*. Its claim to the title of a vegetable alkali, among which class of bodies it was placed by its discoverer, has been called in question by M. Casaseca, from whose remarks it seems that picrotoxia has no alkaline reaction, and does not neutralize acidity. It combines, however, with acids, and with the acetic and nitric acids forms crystallizable compounds. It appears, also, that the menispermic acid, supposed by M. Boullay to be united in the *cocculus indicus* with picrotoxia, is merely a mixture of sulphuric and malic acids. (Edinburgh Journal of Science, No. x.)

*Corydalin.*—This alkali, discovered by Dr Wackenroder, is contained in the root of the fumitory, (not the common fumitory, *fumaria officinalis*, but) *fumaria cava*, and *corydalis tuberosa* of Decandolle. It exists in the plant as a soluble malate, and is precipitated from its aqueous solution in the usual manner, and purified by alcohol.

It is soluble in alcohol, and the hot saturated solution in cooling yields colourless prismatic crystals of a line in length. By spontaneous evaporation fine laminæ are formed. It is likewise soluble in ether, but very sparingly in water. It is insipid and inodorous; but when dissolved by acids or alcohol it is very bitter. Its solution has an alkaline reaction, and it neutralizes acids. Cold dilute nitric acid dissolves it and yields a colourless solution; but when heated it acquires a red tint, and becomes blood-red when concentrated. Its salts are precipitated by potassa, pure or carbonated, and by infusion of gall-

nuts. The precipitate is white when the solution is dilute, and grayish yellow if concentrated. (Philos. Magazine and Annals, iv. 153.).

*Solania.*—The active principle of the *Solanum dulcamara*, or woody nightshade, was procured in a pure state by Desfosses. This compound has distinct alkaline properties, and is combined in the plant with malic acid. (Journal de Pharmacie, vol. vi. and vii.)

*Cynopia.*—Professor Ficinus of Dresden has discovered a new alkali in the *Æthusa Cynapium*, or lesser hemlock, to which he has given the name of *Cynopia*. It is crystallizable, and soluble in water and alcohol, but not in ether. The crystals are in the form of a rhombic prism, which is also that of the crystals of the sulphate.

*Delphia.*—This substance was discovered in the *Delphinium staphysagria*, or *stavesacre*, by MM. Feneuille and Lassaigne. It possesses the general characters of the vegetable alkalies. (An. de Ch. et de Ph. vol. xii.)

*Althea* was announced by M. Bacon of Caen as a new vegetable alkali, said to be procured from the root of the marsh mallow. (Althaea officinalis.) According to M. Plisson, this alkali has no existence, and what was thought to be supermalate of althea is asparagin.

Besides the vegetable alkalies, already described, it has been rendered highly probable, chiefly by the researches of M. Brandes, that several other plants, such as the *Atropa belladonna*, *Conium maculatum*, *Hyoscyamus niger*, *Datura stramonium*, and *Digitalis*, owe their activity to the presence of an alkali.

## SECTION III.

### *SUBSTANCES WHICH, IN RELATION TO OXYGEN, CONTAIN AN EXCESS OF HYDROGEN.*

## *Oils.*

Oils are characterized by a peculiar unctuous feel, by inflammability, and by insolubility in water. They are divided into the fixed and volatile oils, the former of which are comparatively fixed in the fire, and, therefore, give a permanently greasy stain to paper; while the latter, owing to their volatility, produce a stain which disappears by gentle heat.

*Fixed Oils.*—The fixed oils are usually contained in the seeds of plants, as for example in the almond, linseed, rapeseed, and poppy seed; but olive oil is extracted from the pulp which surrounds the stone. They are procured by bruising the seed, and subjecting the pulpy matter to pressure in hempen bags, a gentle heat being generally employed at the same time to render the oil more limpid.

Fixed oils, the palm oil excepted, are fluid at common temperatures, are nearly inodorous, and have little taste. They are lighter than water, their density in general varying from 0.9 to 0.96. They are commonly of a yellow colour, but may be rendered nearly or quite colourless by the action of animal charcoal. At or near the temperature of 600° F, they begin to boil, but suffer partial decomposition at the same time, an inflammable vapour being disengaged even below 500°. When heated to redness in close vessels, a large quantity of the combustible compounds of carbon and hydrogen are formed, together with

the other products of the destructive distillation of vegetable substances; and in the open air they burn with a clear white light, and formation of water and carbonic acid. They may hence be employed for the purposes of artificial illumination, as well in lamps, as for the manufacture of gas.

Fixed oils undergo considerable change by exposure to the air. The rancidity which then takes place is occasioned by the mucilaginous matters which they contain becoming acid. From the operation of the same cause, they gradually lose their limpidity, and some of them, which are hence called *drying* oils, become so dry, that they no longer feel unctuous to the touch nor give a stain to paper. This property, for which linseed oil is remarkable, may be communicated quickly by heating the oil in an open vessel. The drying oils are employed for making oil paint, and mixed with lampblack constitute printers' ink. During the process of drying, oxygen is absorbed in considerable quantity.

The absorption of oxygen by fixed, and especially by drying oils, is under some circumstances so abundant and rapid, and accompanied with such free disengagement of caloric, that light porous combustible materials, such as lampblack, hemp, or cotton-wool, may be kindled by it. Substances of this kind, moistened with linseed oil, have been known to take fire during the space of 24 hours, a circumstance which has repeatedly been the cause of extensive fires in warehouses and in cotton manufactories.

Fixed oils do not unite with water, but they may be permanently suspended in that fluid by means of mucilage or sugar, so as to constitute an *emulsion*. They are for the most part very sparingly soluble in alcohol and ether. Strong sulphuric acid thickens the fixed oils, and forms with them a tenacious matter like soap; and they are likewise rendered thick and viscid by the action of chlorine. Concentrated nitric acid acts upon them with great energy, giving rise in some instances to the production of flame.

Fixed oils unite with the common metallic oxides. Of these compounds, the most interesting is that with the oxide of lead. When linseed oil is heated with a small quantity of litharge, a liquid results which is powerfully drying, and is employed as oil varnish. Olive oil combined with half its weight of litharge forms the common diachylon plaster.

The fixed oils are readily attacked by alkalies. With ammonia, oil forms a soapy liquid, to which the name of *volatile liniment* is applied. The fixed alkalies, boiled with oil or fat, give rise to the soap employed for washing, the soft inferior kind being made with potassa, and the hard with soda. The chemical nature of soap has of late years been elucidated by the labours of M. Chevreul. This chemist has found that fixed oils and fats are not pure proximate principles, but consist of two substances, one of which is solid at common temperatures, while the other is fluid. To the former he has applied the name of stearine from *στεαρ* suet, and to the latter, *eläine* from *ελαιον* oil. Stearine is the chief ingredient of suet, butter, and lard, and is the cause of their solidity; whereas oils contain a greater proportional quantity of eläine, and are consequently fluid. These principles may be separated from one another by exposing fixed oil to a low temperature, and pressing it, when congealed, between folds of bibulous paper. The stearine is thus obtained in a separate form; and by pressing the bibulous paper under water, an oily matter is procured, which is eläine in a state of purity. This principle is peculiarly fitted for greasing the wheels of watches, or other delicate ma-

chinery, since it does not thicken or become rancid by exposure to the air, and requires a cold of about 20° F. for congelation. In the formation of soap, the stearine and elaïne disappear entirely, being converted by a change in the arrangement of their elements into three compounds, to which M. Chevreul* has applied the names of *margaric* and *oleic* acids, and *glycerine*. The two acids enter into combination with the alkali employed, and the resulting compound is soap. A similar change appears to be effected by the action not only of the alkaline earths, but of several of the other metallic oxides.

Soap is decomposed by acids, and by earthy and most metallic salts. On mixing muriate of lime with a solution of soap, a muriate of the alkali is produced, and the lime forms an insoluble compound with the margaric and oleic acids. A similar change ensues when a salt of lead is employed.

According to the analysis of Gay-Lussac and Thenard, 100 parts of olive oil consist of carbon 77.213, oxygen, 9.427, and hydrogen 13.36. From these proportions, it is inferred that olive oil contains ten equivalents of carbon, one of oxygen, and eleven of hydrogen.

*Volatile Oils.*—Aromatic plants owe their flavour to the presence of a *volatile* or *essential* oil, which may be obtained by distillation, water being put into the still along with the plant, in order to prevent the latter from being burned. The oil and water pass over into the recipient, and the oil collects at the bottom or the surface of the water according to its density.

Essential oils have a penetrating odour and acrid taste, which are often pleasant when sufficiently diluted. They are soluble in alcohol, though in different proportions. They are not appreciably dissolved by water; but that fluid acquires the odour of the oil with which it is distilled. With the fixed oils they unite in every proportion, and are sometimes adulterated with them, an imposition easily detected by the mixed oil causing on paper a greasy stain which is not removed by heat.

Volatile oils burn in the open air with a clear white light, and the sole products of the combustion are water and carbonic acid. On exposure to the atmosphere, they gradually absorb a large quantity of oxygen, in consequence of which they become thick, and are at length converted into a substance resembling resin. This change is rendered more rapid by the agency of light.

Of the acids, the action of strong nitric acid on volatile oils is the most energetic, being often attended with vivid combustion,—an effect which is rendered more certain by previously adding to the nitric a few drops of sulphuric acid.

Volatile oils do not unite readily with metallic oxides, and are attacked with difficulty even by the alkalies. The substance called Starkey's soap is made by triturating oil of turpentine with an alkali.

Volatile oils dissolve sulphur in large quantity, forming a deep brown coloured liquid, called *balsam of sulphur*. The solution is best made by boiling flowers of sulphur in spirit of turpentine. Phosphorus may likewise be dissolved by the same menstruum.

The most interesting of the essential oils are those of turpentine, caraway, cloves, peppermint, nutmeg, anise, lavender, cinnamon, citron, and chamomile. Of these the most important is the first, which is much employed in the preparation of varnishes, and for some medical and chemical purposes. It is procured by distilling common

* Recherches sur les Corps gras.

turpentine; and when purified by a second distillation, it is *spirit* or *essence* of turpentine.

Common oil of turpentine is inferred by Dr Ure to consist of fourteen equivalents of carbon, one of oxygen, and ten of hydrogen*. According to M. Houton Labillardière, the purified oil contains no oxygen, but is composed of carbon and hydrogen in such proportions, that one volume of its vapour contains four volumes of olefiant gas, and two volumes of the vapour of carbon†.

*Camphor.*—This inflammable substance, which in several respects is closely allied to the essential oils, exists ready formed in the *Laurus camphora* of Japan, and is obtained from its trunk, root, and branches by sublimation.

Camphor has a bitterish, aromatic, pungent taste, accompanied with a sense of coolness. It is unctuous to the touch, and brittle; but it possesses a degree of toughness which prevents it from being pulverized with facility. It is easily reduced to powder by trituration with a few drops of alcohol. Its specific gravity is 0.988. It is exceedingly volatile, being gradually dissipated in vapour if kept in open vessels. At 288° F. it enters into fusion, and boils at 400° F.

Camphor is insoluble in water; but when triturated with sugar, and then mixed with that fluid, a portion is dissolved sufficient for communicating its flavour. It is dissolved freely by alcohol, and is thrown down by the addition of water. It is likewise soluble in the fixed and volatile oils, and in strong acetic acid. Sulphuric acid decomposes camphor, converting it into a substance like artificial tannin. (Mr Hatchett.) With the nitric it yields camphoric acid.

Camphor, according to the analysis of Dr Ure, appears to consist of ten equivalents of carbon, one equivalent of oxygen, and nine equivalents of hydrogen.

On transmitting a current of dry muriatic acid gas through the purified oil of turpentine, surrounded by a mixture of snow and salt, a quantity of gas is absorbed equal to one-third of the weight of the oil; and a white crystalline substance, very similar to camphor, is generated. This matter was discovered by Kind, and has since been studied by Trommsdorf, Gehlen, and Thenard. The last chemist maintains that this peculiar substance is a compound of turpentine and muriatic acid, a view which is supported by the researches of M. Houton Labillardière.

*Coumarin.*—This name was first applied to the odoriferous principle of the Tonka bean by M. Guibourt, and has since been adopted by MM. Boullay and Boutron-Charlard. (Journal de Pharmacie for October 1825.) It is derived from the term *Coumarouna odorata*, given by Stublet to the plant which yields the bean.

Coumarin is white, of a hot pungent taste, and distinct aromatic odour. It crystallizes sometimes in square needles, and at other times in short prisms. It is moderately hard, fracture clean, lustre considerable, and density greater than that of water. It fuses at a moderate temperature into a transparent fluid, which yields an opake crystalline mass on cooling. Heated in close vessels, it is sublimed without change. It is sparingly soluble in water; but is readily dissolved by ether and alcohol, and the solutions crystallize by spontaneous evaporation. It is very soluble in fixed and volatile oils.

M. Vogel mistook coumarin for benzoic acid; but MM. Boullay

* Philosophical Transactions, for 1822.
† Journal de Pharmacie, vol. iv.

and Boutron-Charlard maintain, that it has neither an acid nor alkaline reaction, and that it is a peculiar independent principle, nearly allied to the essential oils. These chemists did not find any benzoic acid in the Tonka bean, and consider coumarin as the sole cause of its odour.

## *Resins.*

Resins are the inspissated juices of plants, and commonly occur either pure or in combination with an essential oil. They are solid at common temperatures, brittle, inodorous, and insipid. They are non-conductors of electricity, and when rubbed become negatively electric. They are generally of a yellow colour, and semi-transparent.

Resins are fused by the application of heat, and by a still higher temperature are decomposed. In close vessels they yield empyreumatic oil, and a large quantity of carburetted hydrogen, a small residue of charcoal remaining. In the open air, they burn with a yellow flame and much smoke, being resolved into carbonic acid and water.

Resins are dissolved by alcohol, ether and the essential oils, and the alcoholic and ethereal solutions are precipitated by water, a fluid in which they are quite insoluble. Their best solvent is pure potassa and soda, and they are also soluble in alkaline carbonates by the aid of heat. The product is in each case a soapy compound, which is decomposed by an acid.

Concentrated sulphuric acid dissolves resins; but the acid and the resins mutually decompose each other, with disengagement of sulphurous acid, and deposition of charcoal. Nitric acid acts upon them with violence, converting them into a species of tannin, which was discovered by Mr Hatchett. No oxalic acid is formed during the action.

The uses of resin are various. Melted with wax and oil, resins constitute ointments and plasters. Combined with oil or alcohol, they form different kinds of oil and spirit varnish. Sealing-wax is composed of lac, Venice turpentine, and common resin. The composition is coloured black by means of lampblack, or red by cinnabar or red lead. Lampblack is the soot of imperfectly burned resin.

Of the different resins the most important are common resin, copal, lac, sandarach, mastich, elemi, and dragon's blood. The first is procured by heating turpentine, which consists of oil of turpentine and resin, so as to expel the volatile oil. The common turpentine, obtained by incisions made in the trunk of the Scotch fir tree, (*Pinus sylvestris*) is employed for this purpose; but the other kinds of turpentine, such as the Venice turpentine, that from the larch, (*Pinus larix*,) the Canadian turpentine from the *Pinus balsamea*, or the Strasburgh turpentine from the *Pinus picea*, yield resin by a similar treatment.

When turpentine is extracted from the wood of the fir tree by heat, partial decomposition ensues, and a dark substance, consisting of resin, empyreumatic oil, and acetic acid is the product. This constitutes tar; and when inspissated by boiling, it forms pitch. Common resin fuses at 276° F, is completely liquid at 306°, and at about 316°, bubbles of gaseous matter escape, giving rise to the appearance of ebullition. At a red heat, it is entirely decomposed, yielding a large quantity of combustible gas, which is employed for the purpose of artificial illumination. (Page 243.)

Considerable uncertainty prevails as to the composition of common resin, as will appear by the following statement:—

| | *Gay-Lussac and Thenard.* | *Thomson.* | *Ure.* |
|---|---|---|---|
| Carbon | 75.944 | 63.15 | 75.00 |
| Oxygen | 13.337 | 25.26 | 12.50 |
| Hydrogen | 10.719 | 11.59 | 12.50 |
| | 100 | 100 | 100 |

*Amber.*—This substance is found chiefly on the coast of Prussia, Livonia, Pomerania,—and Denmark, occurring sometimes on the shore, and sometimes in beds of bituminous wood. It is undoubtedly of vegetable origin, and has the general properties of a resin; but it differs from resinous substances in yielding succinic acid, when heated in close vessels.

*Balsams.*—The balsams are native compounds of resin and benzoic acid, and issue from incisions made in the trees which contain them, in the same manner as turpentine from the fir. Some of them, such as storax and benzoin, are solid; while others, of which the balsams of Tolu and Peru are examples, are viscid fluids.

*Gum-resins.*—The substances to which this name is applied are the concrete juices of certain plants, and consist of resin, essential oil, gum, and extractive vegetable matter. The two former principles are soluble in alcohol, and the two latter in water. Their proper solvent, therefore, is proof spirit. Under the class of gum-resins are comprehended several valuable medic ines, such as aloes, ammoniacum, assafœtida, euphorbium, galbanu m, gamboge, myrrh, scammony, and guaiacum.

*Caoutchouc*, commonly called elastic gum or Indian rubber, is the concrete juice of the *Hævea caoutchouc* and *Jatropa elastica*, natives of South America, and of the *Ficus indica* and *Artocarpus integrifolia*, which grow in the East Indies. It is a soft yielding solid, of a whitish colour when not blakened by smoke, possesses considerable tenacity, and is particularly remarkable for its elasticity. It is inflammable, and burns with a bright flame. When cautiously heated, it fuses without decomposition. It is insoluble in water and alcohol; but it dissolves, though with some difficulty, in pure ether. It is very sparingly dissolved by the alkalies, but its elasticity is destroyed by their action. By the sulphuric and nitric acids it is decomposed, the former causing deposition of charcoal, and the latter formation of oxalic acid.

Caoutchouc is soluble in the essential oils, in petroleum, and in cajeput oil; and may be procured by evaporation from the two latter without loss of its elasticity. The purified naphtha from coal tar dissolves it readily, and as the solvent is cheap, and the properties of the caoutchouc are unaltered by the process, the solution may be conveniently employed for forming elastic tubes, or other apparatus of a similar kind. It is used by Mr Mackintosh of Glasgow for covering cloth with a thin stratum of caoutchouc, so as to render it impermeable to moisture. This property of coal naphtha was discovered by Mr James Syme, Lecturer on Surgery in Edinburgh. (Annals of Philosophy, vol. xii.*)

* Dr J. K. Mitchell, Lecturer on Chemistry in the Philadelphia Medical Institute, has discovered a mode of making sheet-caoutchouc, which possesses remarkable properties. It is prepared by soaking

The composition of caoutchouc has not been determined in a satisfactory manner. According to the analysis of Dr Ure, 100 parts of it consist of carbon 90, oxygen 0.88, and hydrogen 9.12. But caoutchouc yields ammonia when heated in close vessels, and, therefore, must contain nitrogen as one of its constituents, a principle which was not detected by Dr Ure.

*Wax.*—This substance, which partakes of the nature of a fixed oil, is an abundant vegetable production, entering into the composition of the pollen of flowers, covering the envelop of the plum and other fruits, especially the berries of the *Myrica cerifera*, and in many instances forming a kind of varnish to the surface of leaves. From this circumstance, it was long supposed that wax is solely of vegetable origin, and that the wax of the honey-comb is derived from flowers only; but it appears from the observations of Huber that it must likewise be regarded as an animal product, since he found bees to deposite wax though fed on nothing but sugar.

Common wax is always more or less coloured, and has a distinct peculiar odour, of both which it may be deprived by exposure in thin slices to light, air, and moisture, or more speedily by the action of chlorine. At ordinary temperatures it is solid, and somewhat brittle; but it may easily be cut with a knife, and the fresh surface presents a characteristic appearance, to which the name of waxy lustre is applied. Its specific gravity is 0.96. At about 150° F. it enters into fusion, and boils at a high temperature. Heated to redness in close vessels, it suffers complete decomposition, yielding products very similar to those which are procured under the same circumstances from oil. As it burns with a clear white light, it is employed for forming candles.

Wax is insoluble in water, and is only sparingly dissolved by boiling alcohol or ether, from which the greater part is deposited on cooling.

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the caoutchouc in ether until soft, which generally requires eight or ten hours, and in that state, cutting it into plates or sheets with a wet knife, or stretching it to any desired degree of thinness. If bags of this substance are employed, they may be expanded by means of the breath to the size of between two and three feet in diameter, and become so light as to ascend readily when filled with hydrogen.

Sheet-caoutchouc, prepared by this process, is very soft and pleasant to the touch, possesses great extensibility, and may be made so thin as to appear nearly colourless and transparent, yet retaining considerable strength and tenacity. When two pieces are laid together and cut with scissors, the cut edges adhere with considerable force, and, indeed, after some hours' maceration, unite as strongly as the rest of the sheet. In this way, tubes, bags, socks, caps, &c. both water and air-tight may be formed.

The properties of this preparation are very similar to those of the sheet-caoutchouc, made by Mr Hancock of London. This gentleman conceals his process; but, on the contrary, Dr Mitchell wishes his mode of treating the substance to be generally known.

Dr Mitchell has also discovered a good solvent for caoutchouc. It is the essential oil of sassafras, acting on the substance after it has been softened by ether. A solution of it in this oil, applied to glass or porcelain, will form upon drying a thin pellicle of pure caoutchouc, which, by wetting it with water, can be separated in the form of a sheet. Applied to the surfaces of torn or cut caoutchouc, it causes their firm and inseparable adhesion. *Durand, Journ. of the Phil. College of Pharmacy, Jan.* 1830. B.

It is readily attacked by the fixed alkalies, being converted into a soap which is soluble in hot water. It unites by the aid of heat in every proportion with the fixed and volatile oils, and with resin. With different quantities of oil, it constitutes the simple liniment, ointment, and cerate of the pharmacopœia.

Wax, according to the observations of John, consists of two different principles, one of which is soluble, and the other insoluble in alcohol. To the former he has given the name of *cerin*, and to the latter of *myricin*. From the ultimate analysis of Dr Ure, whose result corresponds closely with that of Gay-Lussac and Thenard, 100 parts of wax are composed of carbon 80.4, oxygen 8.3, and hydrogen 11.3; from which it is probable that it consists of thirteen equivalents of the first element, one equivalent of the second, and eleven equivalents of the third.

## Alcohol.

Alcohol is the intoxicating ingredient of all spirituous and vinous liquors. It does not exist ready formed in plants, but is a product of the vinous fermentation, the theory of which will be stated in a subsequent section.

Common alcohol or spirit of wine is prepared by distilling whisky or some ardent spirit, and the rectified spirit of wine is procured by a second distillation. The first has a specific gravity of about 0.867, and the last of 0.835 or 0.84. In this state it contains a quantity of water, from which it may be freed by the action of substances which have a strong affinity for that liquid. Thus, when carbonate of potassa, heated to about 300° F., is mixed with spirit of wine, the alkali unites with the water forming a dense solution, which on standing, separates from the alcohol, so that the latter may be removed by decantation. To the alcohol, thus deprived of part of its water, fresh portions of the dry carbonate are successively added, until it falls through the spirit without being moistened. Other substances which have a powerful attraction for water, may be substituted for carbonate of potassa. Gay-Lussac recommends the use of pure lime or baryta; (An. de Ch. vol. lxxxvi.) and dry alumina may also be employed with advantage. A very convenient process is to mix the alcohol with chloride of calcium in powder, or with quicklime, and draw off the stronger portion by distillation. Another process which has been recommended for depriving alcohol of water is to put it into the bladder of an ox, and suspend it over a sand bath. The water gradually passes through the coats of the bladder, while the pure alcohol is retained; but though this method answers well for strengthening weak spirit, its power of purifying strong alcohol is very questionable. (Journal of Science, vol. xviii.) The strongest alcohol which can be procured by any of these processes has a specific gravity of 0.796 at 60° F. This is called *absolute* alcohol, on the supposition of its being quite free from water.

An elegant and easy process for procuring absolute alcohol has lately been proposed by Mr Graham. (Edinburgh Philos. Trans. for 1828.) A large shallow basin is covered to a small depth with quicklime in coarse powder, and a smaller one containing three or four ounces of commercial alcohol is supported just above it. The whole is placed upon the plate of an air-pump, covered by a low receiver, and the air withdrawn until the alcohol evinces signs of ebullition. Of the mingled vapours of water and alcohol which fill the receiver, the former alone is absorbed by the quicklime, while the latter is ur

fected. Now it is found that water cannot remain in alcohol, unless covered by an atmosphere of its own vapour; and consequently the water continues to evaporate without interruption, while the evaporation of the alcohol is entirely arrested by the pressure of the vapour of alcohol on its surface. Common alcohol is in this way entirely deprived of water in the course of about five days. The temperature should be preserved as uniform as possible during the process. Sulphuric acid cannot be substituted for quicklime, since both vapours are absorbed by this liquid.

Alcohol is a colourless fluid, of a penetrating odour, and burning taste. It is highly volatile, boiling, when its density is 0.820, at the temperature of 176° F. The specific gravity of its vapour, according to Gay-Lussac, is 1.613. Like volatile liquids in general, it produces a considerable degree of cold during evaporation. It has hitherto retained its fluidity under every degree of cold to which it has been exposed. Mr Hutton, indeed, announced in the 34th volume of Nicholson's Journal, that he had succeeded in freezing alcohol; but the fact itself is regarded as doubtful, since no description of the method has hitherto been published. In the experiments of Mr Walker, alcohol was found to retain its fluidity at —91° F.

Alcohol is highly inflammable, and burns with a lambent yellowish-blue flame. Its colour varies considerably with the strength of the alcohol, the blue tint predominating when it is strong, and the yellow when it is diluted. Its combustion is not attended with the least degree of smoke, and the sole products are water and carbonic acid. When transmitted through a red-hot tube of porcelain, it is resolved into carburetted hydrogen, carbonic oxide, and water, and the tube is lined with a small quantity of charcoal.

Alcohol unites with water in every proportion. The act of combining is usually attended with diminution of volume, so that a mixture of 50 measures of alcohol and 50 of water occupies less than 100 measures. Owing to this circumstance, the action is accompanied with increase of temperature. Since the density of the mixture increases as the water predominates, the strength of the spirit may be estimated by its specific gravity. Equal weights of absolute alcohol and water constitute *proof spirit*, the density of which is 0.917; but the proof spirit employed by the colleges for tinctures has a specific gravity of 0.930, or 0.935.

Of the salifiable bases, alcohol can alone dissolve potassa, soda, lithia, ammonia, and the vegetable alkalies. None of the earths, or other metallic oxides, are dissolved by it. Most of the acids attack it by the aid of heat, giving rise to a class of bodies to which the name of *ether* is applied. All the salts which are either insoluble, or sparingly soluble in water, are insoluble in alcohol. The efflorescent salts are, likewise, for the most part insoluble in this menstruum; but, on the contrary, it is capable of dissolving all the deliquescent salts, except the carbonate of potassa. Many of the vegetable principles, such as sugar, manna, camphor, resins, balsams, and the essential oils, are soluble in alcohol.

The solubility of certain substances in alcohol appears owing to the formation of definite compounds, which are soluble in that liquid. This has been proved of the chlorides of calcium, manganese, and zinc, and of the nitrates of lime and magnesia, by Mr Graham in the essay above cited. It appears from his experiments that all these bodies unite with alcohol in definite proportion, and yield crystalline compounds, which are deliquescent and soluble both in water and alcohol. From their analogy to hydrates, Mr Graham has applied to them the name

of *alcoates*. These are formed by dissolving the substances in absolute alcohol by means of heat, when on cooling a group of crystals more or less irregular is deposited. The salt and alcohol employed for the purpose should be quite anhydrous; for the crystallization is prevented by a very small quantity of water. Estimating the combining proportion of alcohol at 23, the alcoate of chloride of calcium is composed of one equivalent of chloride of calcium, and three equivalents and a half of alcohol. Nitrate of magnesia crystallizes with nine equivalents of alcohol; nitrate of lime with two and a half equivalents; protochloride of manganese with three equivalents; and chloride of zinc with half an equivalent of alcohol.

The constitution of alcohol has been ably investigated by M. Saussure, jun. (An. de Ch. vol. lxxxix.) According to his analysis, which was made by transmitting the vapour of absolute alcohol through a red-hot porcelain tube, and examining the products, this fluid is composed of carbon 51.98, oxygen 34.32, and hydrogen 13.70. From these data, alcohol is inferred to consist of

| | | | |
|---|---|---|---|
| Carbon, | 12 | two equivalents | 52.17 |
| Oxygen, | 8 | one equivalent | 34.79 |
| Hydrogen, | 3 | three equivalents | 13.04 |
| | 23 | | 100.00 |

These numbers, it is obvious, are in such proportion that alcohol may be regarded as a compound of 14 parts or one equivalent of olefiant gas, and 9 parts or one equivalent of water. Hence the equivalent of alcohol is 23.

Knowing the composition of alcohol by weight, it is easy to calculate the proportion of its constituents by measure. For this purpose it is only necessary to divide 14 by 0.972, (the sp. gr. of olefiant gas) and 9 by 0.625, (the sp. gr. of aqueous vapour); and as the quotients are very nearly equal, it follows that alcohol must consist of equal measures of aqueous vapour and olefiant gas. It is inferred, also, that these two gaseous bodies, in uniting to form the vapour of alcohol, occupy half the space which they possessed separately; because the density of the vapour of alcohol, as calculated on this supposition, $(0.9722+0.625=1.5972)$ corresponds closely with 1.613, the number which was ascertained experimentally by Gay-Lussac.

Considerable uncertainty prevailed a few years ago as to the state in which alcohol exists in wine. Some chemists were of opinion that it is generated by the heat employed in the distillation; while others thought that the alcohol is merely separated during the process. This question was finally determined by Mr Brande, who made it the subject of two essays which were published in the Philosophical Transactions for 1811 and 1813. He there demonstrated that the alcohol exists ready formed in wine, by separating that principle without the aid of heat. His method consists in precipitating the acid and extractive colouring matters of the wine by the subacetate of lead, and then depriving the alcohol of water by dry carbonate of potassa, in the way already mentioned. The pure alcohol, which rises to the surface, is then measured by means of a narrow graduated glass tube. The same fact has since been established by the experiments of Gay-Lussac, who procured alcohol from wine by distilling it *in vacuo* at the temperature of 60° F. He also succeeded in separating the alcohol by the method of Mr Brande; but he suggests the employment of litharge in fine powder, instead of the subacetate of lead, for precipitating the colouring matter. (Mem. d'Arcueil, vol. iii.)

The preceding researches of Mr Brande led him to examine the

quantity of alcohol contained in spirituous and fermented liquors. According to his experiments, brandy, rum, gin, and whisky, contain from 51 to 54 per cent of alcohol, of specific gravity 0.825. The stronger wines, such as Lissa, Raisin wine, Marsala, Port, Madeira, Sherry, Teneriffe, Constantia, Malaga, Bucellas, Calcavella and Vidonia, contain from between 18 or 19 to 25 per cent of alcohol. In Claret, Sauterne, Burgundy, Hock, Champagne, Hermitage, and Gooseberry wine, the quantity is from 12 to 17 per cent. In cyder, perry, ale, and porter, the quantity varies from 4 to near 10 per cent. In all spirits, such as brandy or whisky, the alcohol is simply combined with water; whereas in wine it is in combination with mucilaginous, saccharine, and other vegetable principles, a condition which tends to diminish the action of the alcohol upon the system. This may, perhaps, account for the fact that brandy, which contains little more than twice as much real alcohol as good port wine, has an intoxicating power which is considerably more than double.

## *Ether.*

The name *ether* was formerly employed to designate the volatile inflammable liquid which is formed by heating a mixture of alcohol and sulphuric acid; but the same term has since been extended to several other compounds produced by the action of acids on alcohol, and which, from their volatility and inflammability, were supposed to be identical or nearly so with sulphuric ether. It appears, however, from the researches of several chemists, but especially of M. Thenard, that ethers, though analogous in their leading properties, frequently differ both in composition and in their mode of formation. (Mémoires d'Arcueil, vol. i. and ii.)

*Sulphuric Ether.*—In forming this compound, strong sulphuric acid is gently poured upon an equal weight of rectified spirit of wine contained in a thin glass retort, and after mixing the fluids together by agitation, which occasions a free disengagement of caloric, the mixture is heated as rapidly as possible until ebullition commences. At the beginning of the process nothing but alcohol passes over; but as soon as the liquid boils, ether is generated, and condenses in the recipient which is purposely kept cool by the application of ice or moist cloths. When a quantity of ether is collected, equal in general to about half of the alcohol employed, white fumes begin to appear in the retort. At this period, the process should be discontinued, or the receiver changed; for although ether does not cease to be generated, its quantity is less considerable, and several other products make their appearance. Thus on continuing the operation, sulphurous acid is disengaged, and a yellowish liquid, commonly called *ethereal oil* or *oil of wine*, passes over into the receiver. If the heat be still continued, a large quantity of olefiant gas is disengaged, and all the phenomena ensue which were mentioned in the description of that compound. (Page 234.)

Ether, thus formed, is always mixed with alcohol, and generally with some sulphurous acid. To separate these impurities, the ether should be agitated with a strong solution of potassa, which neutralizes the acid, while the water unites with the alcohol. The ether is then distilled by a very gentle heat, and may be rendered still stronger by distillation from the chloride of calcium.

To comprehend the theory of the formation of ether, it is necessary to compare the composition of this substance with that of alcohol. Ether was analyzed by M. Saussure in the same manner as alcohol;

and from the data furnished by his analysis, corrected by Gay-Lussac, (An. de Ch. xcv. 314), ether is inferred to consist of 28 parts or two equivalents of olefiant gas, and 9 parts or one equivalent of water. But alcohol is composed of one equivalent of olefiant gas and one equivalent of water; so that if from two equivalents of alcohol, one of water be withdrawn, the remaining elements are in exact proportion for constituting ether. This is the precise mode in which sulphuric acid is supposed to operate in generating ether, an effect which it is well calculated to produce, owing to its strong affinity for moisture. (Page 181.) This view was first proposed by Fourcroy and Vauquelin, and accounts for the phenomena in a very satisfactory manner. These chemists, it is true, erred in thinking that the sulphuric acid occasions no other change; since subsequent observation has proved that the sulphovinic acid, to the constitution of which sulphuric acid is essential, is formed even at the very commencement of the process. Notwithstanding this error, however, the production of ether may be justly ascribed to the sulphuric acid abstracting water or its elements from the alcohol, an opinion which is supported by various circumstances. Thus it accounts for the disengagement of sulphurous acid and olefiant gas towards the middle and close of the process; for since the elements of the alcohol alone contribute to the formation of ether, while all the sulphuric acid remains in the retort, and most of it in a free state, it is apparent that the relative quantities of alcohol and acid must be continually changing during the operation, until at length the latter predominates so greatly as to be able to deprive the former of all its water, and thus give rise to the disengagement of olefiant gas. (Page 234.) Accordingly it is well known, that if fresh alcohol be added as soon as the production of pure ether ceases, an additional quantity of that substance will be produced. It follows, also, from the same doctrine, that the power of the same portion of acid in forming ether must be limited, because it gradually becomes so diluted with water, that it is at last unable to disunite the elements of the alcohol. Consistently with the same view, it is found that ether, precisely analogous to that from sulphuric acid, may be prepared by digesting alcohol with other acids which have a strong affinity for water, as for example with phosphoric, arsenic, and fluoboric acids.

The production of a peculiar acid in the preceding process was first noticed by M. Dabit, about the year 1800. This substance, to which the name of *sulphovinic* acid is applied, has since been examined by Sertuerner, Vogel, and Gay-Lussac; and the two last mentioned philosophers regarded it as a compound of hyposulphuric acid and a peculiar vegetable matter. Mr Hennel, however, has lately given a different, and to all appearance a more correct view of its nature. According to this chemist, sulphovinic acid and the oil of wine are both composed of sulphuric acid and carburet of hydrogen. The oil of wine, which has no acid reaction when pure, consists of two equivalents of sulphuric acid, eight of carbon, and eight of hydrogen. When heated, it parts with half of its carbon and hydrogen, and sulphovinic acid remains, consisting of two equivalents of sulphuric acid, four of carbon, and four of hydrogen. The oil of wine is a perfectly neutral compound, in which the carburet of hydrogen acts the part of an alkali in neutralizing sulphuric acid. In sulphovinic acid, half the sulphuric acid appears to be neutralized by carburet of hydrogen. (Philos. Trans. for 1826, p. 247, or Journal of Science, xxi. 331.)

Sulphuric ether is a colourless fluid, of a hot pungent taste, and fragrant odour. Its specific gravity in its purest form is about 0.700, or according to Lovitz 0.632; but that of the shops is 0.74 or even

lower, owing to the presence of alcohol. Its volatility is exceedingly great:—Under the atmospheric pressure, ether of density 0.720 boils at 96° or 98° F, and at about 40° F. in a vacuum. (Black's Lectures, vol. i. p. 151.) Its evaporation, from the rapidity with which it takes place, occasions intense cold, sufficient under favourable circumstances for freezing mercury. Its vapour has a density of 2.586. At 46 degrees below zero of Fahr. it is congealed.

Ether combines with alcohol in every proportion, but is very sparingly soluble in water. When agitated with that fluid, the greater part separates on standing, a small quantity being retained, which imparts an ethereal odour to the water. The ether so washed is very pure, because the water retains the alcohol with which it is mixed.

Ether is highly inflammable, burning with a blue flame, and formation of water and carbonic acid. With oxygen gas, its vapour forms a mixture which explodes violently on the approach of flame, or by the electric spark. On being transmitted through a red-hot porcelain tube, it undergoes decomposition, and yields the same product as alcohol.

When a coil of platinum wire is heated to redness, and then suspended above the surface of ether contained in an open vessel, the wire instantly begins to glow, and continues in that state until all the ether is consumed. (Davy.) During this slow combustion, pungent acrid fumes are emitted, which, if received in a separate vessel, condense into a colourless liquid possessed of acid properties. Mr Daniell, who prepared a large quantity of it, was at first inclined to regard it as a new acid, and described it under the name of *lampic acid;* but he has since ascertained that its acidity is owing to the acetic acid, which is combined with some compound of carbon and hydrogen different both from ether and alcohol. (Journal of Science, vol. vi. and xii.)

If ether is exposed to light in a vessel partially filled, and which is frequently opened, it gradually absorbs oxygen, and a portion of acetic acid is generated. This change was first noticed by M. Planche, and has been confirmed by Gay-Lussac. (An. de Ch. et de Ph. ii. 98 and 213.)

The composition of ether by volume may be inferred in the same manner as in the case of alcohol (page 459); namely, by dividing 28 by 0.972, and 9 by 0.625. Ether is thus found to consist of two measures of olefiant gas and one measure of watery vapour; and supposing these three measures, in combining, to contract to one-third of their volume, the specific gravity of the vapour of ether will be $0.972 \times 2 + 0.625 = 2.569$. Now this is so near 2.586, the specific gravity which Gay-Lussac found by actual trial, that the preceding supposition may fairly be admitted.

The solvent properties of ether are less extensive than those of alcohol. It dissolves the essential oils and resins, and some of the vegetable alkalies are soluble in it. It unites also with ammonia; but the fixed alkalies are insoluble in this menstruum.

*Nitrous Ether.*—This compound is prepared by distilling a mixture of concentrated nitric acid with an equal weight of alcohol; but as the reaction is apt to be exceedingly violent, the process should be conducted with extreme care. The safest method is to add the acid to the alcohol by small quantities at a time, allowing the mixture to cool after each addition before more acid is added. The distillation is then conducted at a very gentle temperature, and the ether collected in a Woulfe's apparatus. The theory of the process is in some respects obscure; but as the formation of ether is attended with the disen-

gagement of the protoxide and deutoxide of nitrogen, together with free nitrogen and carbonic acid, it follows that the alcohol and acid mutually decompose eachother. M. Thenard inferred from his experiments, that this ether is a compound of alcohol and nitrous acid; and, consequently, that the essential change during its formation consists in the conversion of nitric into nitrous acid at the expense of one part of the alcohol, while the remainder of that fluid combines with the nitrous acid. Consistently with this view, nitrous ether may be made directly by the action of anhydrous nitrous acid on pure alcohol.

In an essay lately published by MM. Dumas and Boullay, a different opinion has been suggested. According to a careful analysis of nitrous ether, they find it to consist of four equivalents of carbon, five of hydrogen, one of nitrogen, and four of oxygen. These elements are in proportion to constitute two equivalents of olefiant gas, one of water, and one of hyponitrous acid. (An. de Ch. et de Physique, xxxvii. 26.)

The nitrous agrees with sulphuric ether in its leading properties; but it is still more volatile. When recently distilled from quicklime by a gentle heat, it is quite neutral; but it soon becomes acid by keeping. The products of its spontaneous decomposition are alcohol, nitrous acid, and a little acetic acid. A similar change is instantly effected by mixing the ether with water, or distilling it at a high temperature. It is also decomposed by potassa, and, on evaporation, crystals of the nitrite or hyponitrite of that alkali are deposited. (Mémoires d'Arcueil, vol. i.)

*Acetic Ether.*—This ether is analogous in composition to the preceding, and is formed by distilling acetic acid with an equal weight of alcohol. When set on fire, it burns with disengagement of acetic acid; and when mixed with a strong solution of potassa, and subjected to distillation, pure alcohol passes over, and acetate of potassa remains in the retort. It is hence inferred by Thenard to consist of acetic acid and alcohol. When pure it is quite neutral.

According to Thenard, the acetic is the only vegetable acid which forms ether by being heated alone with alcohol. Ether may also be generated by treating the tartaric, oxalic, malic, citric, or benzoic acid with a mixture of alcohol and sulphuric acid, and Thenard regards these ethers as compounds of a vegetable acid with alcohol. But MM. Dumas and Boullay, in the essay above referred to, declare that the elements of all these ethers are in such proportion as to constitute one equivalent of acid, one of water, and two of olefiant gas. They believe them, as also nitrous ether, to be hydrated salts, in which carburet of hydrogen acts the part of an alkali. This view is certainly supported by the observations of Mr. Hennel relative to the oil of wine, and by the constitution of muriatic ether. The employment of sulphuric acid in their formation is likewise favourable to this opinion. The alcohol obtained by distillation with potassa, is supposed by Dumas and Boullay to be generated during the process.

*Muriatic Ether.*—This compound, which is prepared by distilling a mixture of concentrated muriatic acid and pure alcohol, was supposed by Thenard to be analogous in composition to nitrous ether. It appears, however, from the experiments of MM. Robiquet and Colin, that it consists of muriatic acid and the elements of olefiant gas, and is, therefore, quite free from oxygen. (An. de Ch. et de Ph. vol. ii.) It does not affect the colour of litmus paper, volatilizes still more rapidly than sulphuric ether, and is highly inflammable. Its combustion is attended with the disengagement of a large quantity of muriatic acid gas.

*Hydriodic ether*, first prepared by Gay-Lussac, appears to be similar in composition to muriatic ether.

## Bituminous Substances.

Under this title are included several inflammable substances, which, though of vegetable origin, are found in the earth, or issue from its surface. They may be conveniently arranged under the two heads of bitumen and pit-coal. The first comprehends naphtha, petroleum, mineral tar, mineral pitch, asphaltum, and retinasphaltum, of which the three first mentioned are liquid, and the others solid. The second comprises *brown coal*, the different varieties of *common* or *black coal*, and *glance coal*.

*Bitumen.—Naphtha* is a volatile limpid liquid, of a strong peculiar odour, and light yellow colour. Its specific gravity, when highly rectified, is 0.758. It is very inflammable, and burns with a white flame mixed with much smoke. At 186° F. it enters into ebullition, and its vapour has a density of 2 833. (Saussure.) It retains its liquid form at zero of Fahrenheit. It is insoluble in water, and very soluble in alcohol; but it unites in every proportion with sulphuric ether, petroleum, and oils. It appears from the observations of Saussure to undergo no change by keeping, even in contact with air.

Naphtha contains no oxygen, and is hence employed for protecting the more oxidable metals, such as potassium and sodium, from oxidation*. According to the analysis of Saussure, it is composed of carbon and hydrogen in the proportion of six equivalents of the former to five of the latter. Dr Thomson states the composition of naphtha from coal tar, which seems identical with mineral naphtha, to consist of six equivalents of carbon, and six of hydrogen. (Page 240.)

Naphtha occurs in some parts of Italy, and on the banks of the Caspian Sea. It may be procured also by distillation from petroleum.

*Petroleum* is much less limpid than naphtha, has a reddish-brown colour, and is unctuous to the touch. It is found in several parts of Britain and the Continent of Europe, in the West Indies, and in Persia. It occurs particularly in coal districts. The *mineral tar* is very similar to petroleum, but is more viscid and of a deeper colour. Both these species become thick by exposure to the atmosphere, and in the opinion of Mr Hatchett pass into solid bitumen.

*Asphaltum* is a solid brittle bitumen, of a black colour, vitreous lustre, and conchoidal fracture. It melts easily, and is very inflammable. It emits a bituminous odour when rubbed, and by distillation yields a fluid like naphtha. It is soluble in about five times its weight of naphtha, and the solution forms a good varnish. It is rather denser than water.

Asphaltum is found on the surface and on the banks of the Dead Sea, and occurs in large quantity in Barbadoes and Trinidad. It was employed by the ancients in building, and is said to have been used by the Egyptians in embalming.

*Mineral pitch* or *maltha* is likewise a solid bitumen, but is much softer than asphaltum. The elastic bitumen, or *mineral caoutchouc*, is a rare variety of mineral pitch, found only in the Odin mine, near Castleton in Derbyshire.

*Retinasphaltum* is a peculiar bituminous substance, found associated with the brown coal of Bovey in Devonshire, and described by

* See note, page 281. B.

Mr Hatchett in the Philosophical Transactions for 1804. It consists partly of bitumen, and partly of resin, a composition which led Mr Hatchett to the opinion that bitumens are chiefly formed from the resinous principle of plants.

*Pit coal.—Brown coal* is characterized by burning with a peculiar bituminous odour, like that of peat. It is sometimes earthy, but the fibrous structure of the wood from which it is derived is generally more or less distinct, and hence this variety is called *bituminous wood*. *Pitch coal* or jet, which is employed for forming ear-rings and other trinkets, is intermediate between brown and black coal, but is perhaps more closely allied to the former than the latter.

Brown coal is found at Bovey in Devonshire, (Bovey coal); in Iceland, where it is called *surturbrand;* and in several parts of the continent, especially at the Meissner in Hessia, in Saxony, Prussia, and Styria.

Of the *black or common coal* there are several varieties, which differ from each other, not only in the quantity of foreign matters, such as the sulphuret of iron and earthy substances which they contain, but also in the proportion of what may be regarded as essential constituents. Thus some kinds of coal consist almost entirely of carbonaceous matters, and, therefore, form little flame in burning; while others, of which the cannel coal is an example, yield a large quantity of inflammable gases by heat, and consequently burn with a large flame. Dr Thomson has arranged the different kinds of coal which are met with in Britain into four subdivisions. (An. of Phil. vol. xiv.) The first is *caking coal*, because its particles are softened by heat and adhere together, forming a compact mass. The coal found at Newcastle, around Manchester, and in many other parts of England, is of this kind. The second is termed *splint coal*, from the splintery appearance of its fracture. The *cherry coal* occurs in Staffordshire, and in the neighbourhood of Glasgow. Its structure is slaty, and it is more easily broken than the splint coal, which is much harder. It easily takes fire, and is consumed rapidly, burning with a clear yellow flame. The fourth kind is the *cannel coal*, which is found of peculiar purity at Wigan in Lancashire. In Scotland it is known by the name of *parrot coal*. From the brilliancy of the light which it emits while burning, it is sometimes used as a substitute for candles, a practice which is said to have led to the name of *cannel* coal. It has a very compact structure, does not soil the fingers when handled, and admits of being polished. Snuff-boxes and other ornaments are made with this coal; and it is peculiarly well fitted for forming coal gas. According to the experiments of Dr Thomson, these varieties of coal are thus constituted:

| | *Caking Coal.* | *Splint Coal.* | *Cherry Coal.* | *Cannel Coal.* |
|---|---|---|---|---|
| Carbon, | 75.28 | 75.00 | 74.45 | 64.72 |
| Hydrogen, | 4.18 | 6.25 | 12.40 | 21.56 |
| Nitrogen, | 15.96 | 6.25 | 10.22 | 13.72 |
| Oxygen, | 4.58 | 12 50 | 2.93 | 0.00 |
| | 100.00 | 100.00 | 100.00 | 100.00 |

Judging from the quantity of oxidized products (water, carbonic acid, and carbonic oxide,) which are procured during the distillation of coal, Dr Henry infers that coal contains more oxygen than was found by Thomson. (Elements, 10th Edition, vol. ii. p. 321.) This opinion is supported by the analysis of Dr Ure, who found 26.6 per cent of oxygen in splint, and 21.9 in cannel coal. When coal is heated

to redness in close vessels, a great quantity of volatile matter is dissipated, and a carbonaceous residue, called *coke*, remains in the retort. The volatile substances are coal tar, acetic acid, water, sulphuretted hydrogen, and hydrosulphuret and carbonate of ammonia, together with the several gases formerly enumerated. (Page 241.) The greater part of these substances are real products, that is, are generated during the distillation. The bituminous matters probably exist ready formed in coal; but Dr Thomson is of opinion that these are also products, and that coals are atomic compounds of carbon, hydrogen, nitrogen, and oxygen.

*Glance Coal.*—Glance coal, or *anthracite*, differs from common coal, which it frequently accompanies, in containing no bituminous substances, and in not yielding inflammable gases by distillation. Its sole combustible ingredient is carbon, and consequently it burns without flame. It commonly occurs in the immediate vicinity of basalt, under circumstances which lead to the suspicion that it is coal from which the volatile ingredients have been expelled by subterranean heat. At the Meissner, in Hessia, it is found between a bed of brown coal and basalt. The Kilkenny coal appears to be a variety of glance coal. (Thomson, An. of Phil. vol. xv.)

## SECTION IV.

### *SUBSTANCES, THE OXYGEN AND HYDROGEN OF WHICH ARE IN EXACT PROPORTION FOR FORMING WATER.*

### *Sugar.*

Sugar is an abundant vegetable product, existing in a great many ripe fruits, though few of them contain it in sufficient quantity for being collected. The juice which flows from incisions made in the trunk of the American maple tree, is so powerfully saccharine that it may be applied to useful purposes. Sugar was prepared in France and Germany during the late war from the beet-root; and this manufacture is at present carried on in France on a scale of considerable magnitude. Proust extracted it in Spain from grapes. But nearly all the sugar at present used in Europe is obtained from the sugar-cane, (*Arundo saccharifera*) which contains it in greater quantity than any other plant. The process, as practised in our West India Islands, consists in evaporating the juice of the ripe cane by a moderate and cautious ebullition, until it has attained a proper degree of consistence for crystallizing. During this operation lime-water is added, partly for the purpose of neutralizing free acid, and partly to facilitate the separation of extractive and other vegetable matters, which unite with the lime and rise as a scum to the surface. When the syrup is sufficiently concentrated, it is drawn off into shallow wooden coolers, where it becomes a soft solid composed of loose crystalline grains. It is then put into barrels with holes in the bottom, through which a black ropy juice, called molasses or treacle, gradually drops, leaving the crystallized sugar comparatively white and dry. In this state it constitutes the raw or muscovado sugar.

Raw sugar is further purified by boiling a solution of it with white

of eggs, or the serum of bullock's blood, lime-water being generally employed at the same time. When properly concentrated, the clarified juice is received in conical earthen vessels, the apex of which is undermost, in order that the fluid parts may collect there, and be afterwards drawn off by the removal of a plug. In this state it is loaf or refined sugar. In the process of refining sugar, it is important to concentrate the syrup at a low temperature; and on this account a very great improvement was introduced some years ago by conducting the evaporation in *vacuo*.

Pure sugar is solid, white, inodorous, and of a very agreeable taste. It is hard and brittle, and when two pieces are rubbed against each other in the dark, phosphorescence is observed. It crystallizes in the form of four or six-sided prisms bevelled at the extremities. The crystals are best made by fixing threads in syrup, which is allowed to evaporate spontaneously in a warm room; and the crystallization is promoted by adding spirit of wine. In this state it is known by the name of *sugar-candy*.

Sugar undergoes no change on exposure to the air; for the deliquescent property of raw sugar is owing to impurities. It is soluble in an equal weight of cold, and to almost any extent in hot water. It is soluble in about four times its weight of boiling alcohol, and the saturated solution, by cooling and spontaneous evaporation, deposites large crystals. When the aqueous solution of sugar is mixed with yeast, it undergoes the vinous fermentation, the theory of which will be explained in a subsequent section.

Sugar unites with the alkalies and alkaline earths, forming compounds in which the taste of the sugar is greatly injured; but it may be obtained again unchanged by neutralizing with sulphuric acid, and dissolving the sugar in alcohol. When boiled with the oxide of lead, it forms an insoluble compound, which consists of 58.26 parts of the oxide of lead, and 41.74 parts of sugar, (Berzelius); but it is not precipitated by the acetate or subacetate of lead.

Sulphuric acid decomposes sugar with deposition of charcoal; and nitric acid causes the production of oxalic acid, as already described in a former section. The vegetable acids diminish the tendency of sugar to crystallize.

Sugar is very easily affected by heat, acquiring a dark colour and burned flavour. At a high temperature, it yields the usual products of the destructive distillation of vegetable matter, together with a considerable quantity of pyromucic acid.

The analyses of sugar by different chemists are considerably discordant. This is accounted for not only by errors of manipulation, and impurity in the materials; but in part arises, according to Dr Prout, from difference in composition. In his Essay on Alimentary Substances, published in the Philosophical Transactions for 1827, page 355, he states that pure cane sugar, as exemplified in sugar-candy and the best loaf sugar, well dried at 212° F, consists of 42.85 parts of carbon, and 57.15 of oxygen, and hydrogen in the proportion for forming water; while sugar from honey contains only 36.36 per cent of carbon. He considers the sugar from starch, diabetic urine, and grapes, to be nearly the same as that from honey. The sugar from the maple tree and beet-root corresponds with that from the cane; but the quantity of carbon in these kinds of sugar appears to vary from 40 to 42.85 per cent. The atomic constitution of sugar is unknown; but from a former analysis of Dr Prout, it is thought that its elements are in the ratio of 6 parts or one equivalent of carbon to 9 parts or one equivalent

of water, or by volume of one measure of the vapour of carbon to one measure of aqueous vapour. This estimate is admitted by most chemists.

*Molasses.*—The saccharine principle of treacle has been supposed to be different from crystallizable sugar; but it more probably consists of common sugar, which is prevented from crystallizing by the presence of foreign substances, such as saline, acid, and other vegetable matters.

*Sugar of Grapes.*—The sugar procured from the grape has the essential properties of common sugar. Its taste, however, is not so sweet as common sugar, and according to Saussure and Prout, it differs slightly in composition, containing a smaller quantity of carbon. The saccharine principle of the acidulous fruits has not been particularly examined. It is obtained with difficulty in a pure state, owing to the presence of vegetable acids, which prevent it from crystallizing.

A saccharine substance similar to that from grapes may be procured from several vegetable principles, such as starch and the ligneous fibre, by the action of sulphuric acid.

*Honey.*—According to Proust, honey consists of two kinds of saccharine matter, one of which crystallizes readily and is analogous to common sugar, while the other is uncrystallizable. They may be separated by mixing honey with alcohol, and pressing the solution through a piece of linen. The liquid sugar is removed, and the crystallizable portion is left in a solid state. Besides sugar, it contains mucilaginous, colouring, and odoriferous matter, and probably a vegetable acid. Diluted with water, honey is susceptible of the vinous fermentation without the addition of yeast.

The natural history of honey is as yet imperfect. It is uncertain whether honey is merely collected by the bee from the nectaries of flowers, and then deposited in the hive unchanged, or whether the saccharine matter of the flower does not undergo some change in the body of the animal.

*Manna.*—This saccharine matter is the concrete juice of several species of ash, and is procured in particular from the *Fraxinus ornus.* The sweetness of manna is owing, not to sugar, but to a distinct principle called *mannite,* which is mixed with a peculiar vegetable extractive matter. Manna is soluble both in water and boiling alcohol, and the latter, on cooling, deposites pure mannite in the form of minute acicular crystals, which are often arranged in concentrical groups. Mannite differs from sugar, in not fermenting when mixed with water and yeast. According to Dr Prout, it contains 38.7 per cent of carbon, and 61.3 of oxygen, and hydrogen in the proportion to form water.

## *Starch or Fecula.—Amidine.*

Starch exists abundantly in the vegetable kingdom, being one of the chief ingredients of most varieties of grain, of some roots, such as the potato, and of the kernels of leguminous plants. It is easily procured by letting a small current of water fall upon the dough of wheat flour inclosed in a piece of linen, and subjecting it at the same time to pressure between the fingers, until the liquid passes off quite clear. The gluten of the flour is left in a pure state, the saccharine and mucilaginous matters are dissolved, and the starch is washed away mechanically, being deposited from the water on standing in the form of

a white powder. An analogous process is practised on a large scale in the preparation of the starch of commerce; and very pure starch may also be obtained in a similar manner from the potato.

Starch is insipid and inodorous, of a white colour, and insoluble in alcohol, ether, and cold water. It does not crystallize; but is commonly found in the shops in six-sided columns of considerable regularity, a form occasioned by the contraction which it suffers in drying. Boiling water acts upon it readily, converting it into a tenacious bulky jelly, which is employed for stiffening linen. In a large quantity of hot water, it is dissolved completely, and is not deposited on cooling. The aqueous solution is precipitated by subacetate of lead; but the best test of starch, by which it is distinguished from all other substances, is iodine. This principle forms a blue compound with starch, whether in a solid state or when dissolved in cold water.

Starch unites with the alkalies, forming a compound which is soluble in water, and from which the starch is thrown down by acids. Strong sulphuric acid decomposes it. Nitric acid in the cold dissolves starch; but converts it by the aid of heat into the oxalic and malic acids.

The effects of heat on starch are peculiar, and have lately been examined by M. Caventou. (An. de Chim. et de Ph. vol. xxxi.) On exposing dry starch to a temperature a little above 212° F. it acquires a slightly red tint, emits an odour of baked bread, and is rendered soluble in cold water. Starch suffers a similar modification by the action of hot water. Gelatinous starch is generally supposed to be a hydrate of starch; but M. Caventou maintains that the jelly cannot by any method be restored to its original state. He regards this modified starch as identical with the substance described by Saussure under the name of *amidine.* Saussure thought it was generated by exposing a paste made with starch and water for a long time to the air; but according to Caventou, the amidine was formed by the action of the hot water on starch in making the paste. Its essential character is to yield a blue colour with iodine, and to be soluble in cold water. When the solution is gently evaporated to dryness, it yields a transparent mass like horn, which retains its solubility in cold water. When starch is exposed to a still higher temperature than is sufficient for converting it into amidine, a more complete change is effected. It now dissolves with much greater facility in cold water, and gives a purple colour to iodine. A similar effect is produced by long continued boiling. To torrefied starch, that is, starch modified by heat, whether in the dry way or by boiling water, the term *amidine* may be applied.

The starch from wheat, according to the analysis of Gay-Lussac and Thenard, is composed, in 100 parts, of carbon 43.55, oxygen 49.68, and hydrogen 6.77; and this result agrees with the analysis of potato starch made by Berzelius. The results of Prout and Marcet correspond closely with the foregoing. The proportion of the constituents of starch is therefore very analogous to that of sugar, a circumstance which will account for the conversion of the former into the latter. This change is effected in seeds at the period of germination, and is particularly exemplified in the process of malting barley, during which the starch of that grain is converted into sugar. Proust* finds that barley contains a peculiar principle which he calls *hordein,* and which he conceived to be converted in malting partly into starch, and

* An. de Ch. et de Ph. vol. v.

partly into sugar. Dr Thomson is of opinion that hordein should rather be regarded as a modification of starch than as a distinct proximate principle*. A similar conversion of starch into sugar appears in some instances to be the effect of frost, as in the potato, apple, and parsnip.

If starch is boiled for a considerable time in water acidulated with 1-12th of its weight of sulphuric acid, it is wholly converted into a saccharine matter similar to that of the grape. This fact was first observed by Kirchoff, and has since been particularly examined by Vogel, De la Rive, and Saussure. It has been established by Saussure that the oxygen of the air exerts no influence over the process, that no gas is disengaged, that the quantity of acid suffers no diminution, and that 100 parts of starch yield 110.14 of sugar. By careful analysis, he found that the only difference in the composition of the starch and sugar is, that the latter contains more of the elements of water than the former. He hence inferred that the starch is converted into sugar by its elements combining with a certain quantity of oxygen and hydrogen in the proportion to form water; and that the acid acts only by increasing the fluidity of the mass. (Ann. of Philosophy, vol. vi.) Saussure also found that a large quantity of saccharine matter is produced, when gelatinous starch or amidine is kept for a long time either with or without the access of air. (An. de Ch. et de Ph. vol. xi.)

The recent researches of M. Caventou, already referred to, have thrown considerable light on the chemical nature of several of the amylaceous principles of commerce. *The Indian arrow root*, which is prepared from the root of the *Maranta arundinacea*, has all the characters of pure starch. Sago, obtained from the pith of an East Indian palm tree, (*Cycas circinalis*) and tapioca, from the root of the *Iatropha manihot*, are chemically the same substance. They both exist in the plants from which they are extracted, in the form of starch; but as heat is employed in their preparation, the starch is more or less completely converted into amidine. It hence follows that pure potato starch may be used instead of arrow root, and that the same material, modified by heat, would afford a good substitute for sago and tapioca. Salep, which is obtained from the *Orchis mascula*, consists almost entirely of the substance called *bassorin*, together with a small quantity of gum and starch.

## Gum.

Gum is a common proximate principle of vegetables, and is not confined to any particular part of plants. The purest variety is the gum arabic, the concrete juice of several species of the *Mimosa* or *Acacia*, natives of Africa and Arabia.

Gum arabic occurs in small, rounded, transparent, friable grains, commonly of a pale yellow colour, inodorous, and nearly tasteless. It softens when put into water, and then dissolves, forming a viscid solution called *mucilage*. It is insoluble in alcohol and ether, and the former precipitates gum from its solution in water in the form of opake white flakes. It is soluble both in alkaline solutions and in lime-water, and is precipitated unchanged by acids. The dilute acids dissolve, and the concentrated acids decompose gum. Sulphuric acid causes the formation of water and acetic acid, and deposition of char-

* Annals of Philosophy, vol. x.

coal. Digested with strong nitric acid, it yields saccholactic acid, a property which forms a good character for gum. The malic and oxalic acids are generated at the same time.

The aqueous solution of gum may be preserved a considerable time without alteration; but at length it becomes sour, and exhales an odour of acetic acid; a change which takes place without exposure to the air, and must, therefore, be owing to a new arrangement of its own elements.

Gum is precipitated from its solution in water by several metallic salts, and especially by the subacetate of lead, which occasions a curdy precipitate, consisting of 38.25 parts of the oxide of lead, and 61.75 parts of gum. (Berzelius.)

When gum is heated to redness in close vessels, it yields, in addition to the usual products, a small quantity of ammonia, which is probably derived from some impurity. It affords a large residue of ash, when burned, which amounts to three per cent, and consists chiefly of the carbonate, together with some phosphate of lime, and a little iron.

From the analysis of Gay-Lussac and Thenard, it appears that 100 parts of gum arabic consist of carbon 42.23, oxygen, 50.84, and hydrogen 6.93. This result corresponds very closely with that of Berzelius.

Besides gum arabic there are several well-marked kinds of this principle, especially the gum tragacanth, cherry-tree gum, and the mucilage from linseed. All these varieties, though distinguishable from one another by some peculiarity, have the common character of yielding the saccholactic by the action of nitric acid. (Dr Bostock in Nicholson's Journal, vol. xviii.) The substance called *vegetable jelly*, such as is derived from the currant, appears to be mucilage or some modification of gum combined with vegetable acid.

A substance very analogous to vegetable jelly, if not identical with it, has been described by M. Braconnot as a distinct acid under the name of *pectic acid*, (from πηκτὶς coagulum), indicative of its tendency to gelatinize. M. Braconnot believes it to be present in all plants; but extracts it chiefly from the carrot. The original account of its properties appears to have been exaggerated, and its claim to be regarded as an independent proximate principle has not yet been clearly established. (An. de Ch. et Ph. xxviii. 173.)

## Lignin.

*Lignin* or *woody fibre* constitutes the fibrous structure of vegetable substances, and is the most abundant principle in plants. The different kinds of wood contain about 96 per cent of lignin. It is prepared by digesting the sawings of any kind of wood successively in alcohol, water, and dilute muriatic acid, until all the substances soluble in these menstrua are removed.

Lignin has neither taste nor odour, undergoes no change by keeping, and is insoluble in alcohol, water, and the dilute acids. By digestion in a concentrated solution of pure potassa, it is converted, according to M. Braconnot, into a substance similar to ulmin. Mixed with strong sulphuric acid, it suffers decomposition, and is changed into a matter resembling gum; and on boiling the liquid for some time, the mucilage disappears, and a saccharine principle like the sugar of grapes is generated. M. Braconnot finds that several other substances which consist chiefly of woody fibre, such as straw, bark, or linen, yield sugar by a similar treatment. (An. de Ch. et de Ph. vol. xii.)

Digested in nitric acid, lignin is converted into the oxalic, malic, and acetic acids.

When the woody fibre is heated in close vessels, it yields a large quantity of impure acetic acid, (pyroligneous acid), and charcoal of great purity remains in the retort. During this process, a peculiar spirituous liquid is formed, which was discovered in 1812 by Mr P. Taylor*, and has been examined by MM. Macaire and Marcet†, who proposed for it the name of *pyroxylic spirit*. This liquid is similar to alcohol in several of its properties, but differs from it essentially in not yielding ether by the action of sulphuric acid. It has a strong, pungent, ethereal odour, with a flavour like the oil of peppermint. It boils at 150° F. and its density is 0.828. It burns with a blue flame, and without residue. The pyroacetic spirit, obtained by Mr Chenevix by distilling the acetates of manganese, zinc, and lead, differs from the pyroxylic spirit, not only in composition, but in burning with a yellow flame, and in being miscible in all proportions with the oil of turpentine. Pyroxylic spirit, according to the analysis of Macaire and Marcet, consists of carbon, oxygen, and hydrogen, very nearly in the proportion of six equivalents of the first, four of the second, and seven of the third; and the pyroacetic spirit, of four equivalents of carbon, two of oxygen, and three of hydrogen. The pyroacetic spirit appears very similar, if not identical with the pyroacetic ether of Derosne; and, like the pyroxylic spirit, differs essentially from alcohol in not yielding ether by the action of sulphuric acid. (Page 427.)

The ligneous fibre was found by Gay-Lussac and Thenard to consist of carbon 51.43, oxygen 42.73, and hydrogen 5.82. According to Dr Prout it contains 50 per cent of carbon.

## SECTION V.

### *SUBSTANCES WHICH, SO FAR AS IS KNOWN, DO NOT BELONG TO EITHER OF THE PRECEDING SECTIONS.*

### *Colouring Matter.*

Infinite diversity exists in the colour of vegetable substances; but the prevailing tints are red, yellow, blue, and green, or mixtures of these colours. The colouring matter rarely or never occurs in an insulated state, but is always attached to some other proximate principle, such as mucilaginous, extractive, farinaceous, or resinous substances, by which some of its properties, and in particular that of solubility, is greatly influenced. Nearly all kinds of vegetable colouring matter are decomposed by the combined agency of the sun's rays and a moist atmosphere; and they are all, without exception, destroyed by chlorine. (Page 197.) Heat, likewise, has a similar effect, even without being very intense; for a temperature between 300° or 400° F. aided by moist air, destroys the colouring ingredient. Acids and alkalies com-

* Quarterly Journal, vol. xiv. p. 436.

† Annals of Philosophy, N.S. vol. viii. p. 69.

monly change the tint of vegetable colours, entering into combination with them, so as to form new compounds.

Several of the metallic oxides, and especially alumina and the oxides of iron and tin, form with colouring matter insoluble compounds, to which the name of *lakes* is applied. Lakes are commonly obtained by mixing alum or the muriate of the peroxide of tin with a coloured solution, and then by means of an alkali precipitating the oxide which unites with the colour at the moment of separation. On this property are founded many of the processes in dyeing and calico-printing. The art of the dyer consists in giving a uniform and permanent colour to cloth. This is sometimes effected merely by immersing the cloth in the coloured solution; whereas in other instances the affinity between the colour and the fibre of the cloth is so slight, that it only receives a stain which is removed by washing with water. In this case some third substance is requisite, which has an affinity both for the cloth and colouring matter, and which, by combining at the same time with each, may cause the dye to be permanent. A substance of this kind was formerly called a *mordant*, but the term *bases*, introduced by the late Mr Henry of Manchester, is now more generally employed. The most important bases, and indeed the only ones in common use, are alumina, oxide of iron, and oxide of tin. The two former are exhibited in combination either with the sulphuric or acetic acid, and the latter most commonly as the muriate. Those colouring substances that adhere to the cloth without a basis are called *substantive* colours, and those which require a basis, *adjective* colours.

Various as are the tints observable in dyed stuffs, they may all be produced by the four simple ones, blue, red, yellow, and black; and hence it will be convenient to treat of colouring matters in that order.

*Blue Dyes.*—Indigo is the chief substance employed for giving the blue dye. The best indigo is obtained from an American and Asiatic plant, the *Indigofera*, but an inferior sort has also been prepared from the *Isatis tinctoria*, or *woad*, a native of Europe. The plant is cut a short time before its flowering, and is put into large vats covered with water, when fermentation spontaneously ensues, during which the indigo subsides in the form of a pulverulent pulpy matter. Its colour is at first green; but by exposure to the air, it absorbs oxygen and becomes blue.

Indigo is a light brittle substance, of a deep blue colour, and without either taste or odour. At 550° F. it sublimes, forming a violet vapour with a tint of red, and condensing into long flat acicular crystals, which appear red by reflected, and blue by transmitted light. The process of subliming indigo is one of considerable delicacy, owing to the circumstance that the temperature at which it sublimes is very near that at which it is decomposed. Sublimation, however, affords the best method of procuring indigo in a state of perfect purity, and minute directions have been given by Mr Crum for conducting it with success. (An. of Phil. N. S. vol. v.)

Indigo in its dry state may be preserved without change; but when kept under water, it is gradually decomposed. It is quite insoluble in water and alcohol, and is attacked by the alkalies in a partial manner. Its only proper solvent is concentrated sulphuric acid. When indigo is put into this acid, a yellow solution is at first formed, which, after a few hours, acquires a deep blue colour. If the indigo is pure, sulphurous acid is not generated, nor is the acid decomposed; but the indigo undergoes a change, for it is rendered soluble in water. To the indigo thus modified Mr Crum has applied the name of *cerulin*, and he regards it as a compound of one equiva-

lent of indigo, and four of water. This solution, properly diluted with water, is employed by dyers for forming what is called the *Saxon blue.* Mr Crum has also described another compound of indigo and water, under the name of *phenecin,* from φοινιξ purple, because it acquires a purple colour on the addition of a salt. It appears to consist of one equivalent of indigo, and two of water.

When indigo, suspended in water, is brought into contact with certain deoxidizing agents, it is deprived of oxygen, becomes green, and is rendered soluble in water, and still more so in the alkalies. This effect is produced, for example, by sulphuretted hydrogen, by the hydrosulphuret of ammonia, by the protoxide of iron precipitated by lime or potassa, or by a solution of the sulphuret of arsenic in potassa. On dipping cloth into a solution of deoxidized indigo, it receives a green tint, which becomes blue by exposure to the air. This is the usual method of dyeing blue by means of indigo, a colour which adheres permanently to cloth without the intervention of a basis.

From the analytical researches of Mr Crum, it appears that indigo is composed of nitrogen, oxygen, hydrogen, and carbon, in the proportion of one equivalent of the first element, two of the second, four of the third, and sixteen of the fourth. This would make its atomic weight 130.

*Red Dyes.*—The chief substances which are employed for giving the red dye are cochineal, archil, madder, Brazil wood, logwood, and safflower, all of which are adjective colours. The cochineal is obtained from an insect which feeds upon the leaves of several species of the *cactus,* and which is supposed to derive this colouring matter from its food. It is very soluble in water, and is fixed on cloth by means of alumina or the oxide of tin. Its natural colour is crimson; but when the bitartrate of potassa is added to the solution, it yields a rich scarlet dye. The beautiful pigment called *carmine,* is a lake made of cochineal and alumina, or the oxide of tin.

The dye called *archil* is obtained from a peculiar kind of lichen, (*Lichen roccella,*) which grows chiefly in the Canary Islands, and is employed by the Dutch in forming the blue pigment called *litmus* or *turnsol.* The colouring ingredient of litmus is a compound of the red colouring matter of the lichen and an alkali; and hence, on the addition of an acid, the colouring matter is set free, and the red tint of the plant is restored. Litmus is not only used as a dye, but is employed by chemists for detecting the presence of a free acid.

The colouring principle of logwood has been procured in a separate state by M. Chevreul, who has applied to it the name of *hematin.* (An. de Ch. vol. lxxxi.) It is obtained in crystals by digesting the aqueous extract of logwood in alcohol, and allowing the alcoholic solution to evaporate spontaneously.

The safflower is the dried flowers of the *Carthamus tinctorius,* which is cultivated in Egypt, Spain, and in some parts of the Levant. The pigment called *rouge* is prepared from this dye. Madder is the root of the *Rubia tinctorum.*

*Yellow Dyes.*—The chief yellow dyes are the quercitron bark, turmeric, wild American hiccory, fustic, and saffron. They are all adjective colours. The quercitron bark, which is one of the most important of the yellow dyes, was introduced into notice by Dr Bancroft. With a basis of alumina, the decoction of this bark gives a bright yellow dye. With the oxide of tin, it communicates a variety of tints which may be made to vary from a pale lemon colour to deep orange. With the oxide of iron it gives a drab colour.

Turmeric is the root of the *Curcuma longa,* a native of the East

Indies. Paper stained with a decoction of this substance constitutes the *turmeric* or *curcuma* paper, employed by chemists as a test of free alkali, by the action of which it receives a brown stain.

The colouring ingredient of saffron (*Crocus sativus*) is soluble in water and alcohol, has a bright yellow colour, is rendered blue and then lilac by sulphuric acid, and receives a green tint on the addition of nitric acid. From the great diversity of colours which it is capable of assuming under different circumstances, MM. Bouillon Lagrange and Vogel have proposed for it the name of *polychroite*. (An. de Ch. vol. lxxx.)

*Black Dyes.*—The black dye is made of the same ingredients as writing ink, and therefore consists essentially of a compound of the oxide of iron with gallic acid and tannin. From the addition of logwood and acetate of copper, the black receives a shade of blue.

By the dexterous combination of the four leading colours, blue, red, yellow, and black, all other shades of colour may be procured. Thus green is communicated by forming a blue ground with indigo, and then adding a yellow by means of quercitron bark.

The reader who is desirous of studying the details of dyeing and calico-printing, a subject which does not fall within the plan of this work, may consult Berthollet's *Eléments de l'Art de la Teinture;* the treatise of Dr Bancroft on Permanent Colours; a paper by Mr Henry in the third volume of the Manchester Memoirs; and the Essay of Thenard and Roard in the 74th volume of the *Annales de Chimie.*

## *Tannin.*

Tannin exists in large quantity in the excrescences of several species of the oak, called *gall-nuts;* in the bark of most trees; in some inspissated juices, such as kino and catechu; in the leaves of the tea-plant, sumach, whortleberry, (*Uva ursi,*) and in all astringent plants, being the chief cause of the astringency of vegetable matter. It is frequently associated with gallic acid, as for example in gall-nuts, most kinds of bark, and in tea; but in kino, catechu, and cinchona bark, no gallic acid is present. In some instances, tannin appears to be converted into gallic acid. Thus on exposing an infusion of gall-nuts for some time to the air, nearly all the tannin disappears, and a quantity of gallic acid is found in the liquid much greater than what it had originally contained. (Page 439.)

Several processes have been recommended for the preparation of tannin; but it is doubtful if it has ever, by these methods, been obtained in a pure state. Owing to this circumstance, the nature and composition of tannin is involved in obscurity. Proust proposes to prepare tannin by pouring muriate of tin into a concentrated solution of Aleppo galls, until the yellowish precipitate, which at first falls, ceases to appear. The precipitate is washed with a small quantity of cold water, and then dissolved in warm water, through which a current of sulphuretted hydrogen gas is transmitted, in order to precipitate the tin. From the clear liquid, after being filtered, the tannin, mixed with a little gallic acid and extractive matter, is procured by gentle evaporation.

Tannin, in its dry state, is a brown friable substance, of a resinous fracture, insoluble in pure alcohol, but soluble in water. The aqueous solution has a deep brown colour, and is said not to become mouldy by keeping. It has a strong attraction both for acids and alkalies, forming compounds which are, for the most part, of sparing solubility in water.

Thus the sulphuric, muriatic, and most other acids, added to a solution of gall-nuts, cause a precipitate, which is tannin combined with a portion of acid. The alkaline bases have a similar effect. Tannin is precipitated, for example, by the carbonates of potassa and ammonia, by the alkaline earths, by alumina, and many of the oxides of the common metals. Nitric acid and chlorine decompose tannin, producing a change, the nature of which is not well understood.

The most characteristic property of tannin is its action on a salt of iron and a solution of gelatin. With the peroxide of iron, or still better with the protoxide and peroxide mixed, tannin forms a black-coloured compound, which, together with the gallate of iron, constitutes the basis of writing ink and the black dyes. (Page 475.) Mixed with a solution of gelatin, a yellowish flocculent precipitate subsides, which is insoluble in water, resists putrefaction powerfully, and on drying becomes hard and tough. This substance, to which the name of *tanno-gelatin* has been applied, is the essential basis of leather, being always formed when skins are macerated in an infusion of bark. The composition of tanno-gelatin is not always uniform, having been found by Dr Duncan, jun. and Dr Bostock to vary with the proportions employed. If the gelatin is added in slight excess only, the resulting compound consists, according to Sir H. Davy, of 54 parts of gelatin and 46 of tannin; so that the quantity of tannin contained in any fluid may in this way be determined with tolerable precision. Tanno-gelatin is soluble to a considerable extent in an excess of gelatin.

From an analysis of the compound of tannin and oxide of lead, Berzelius states that 100 parts of tannin are composed of carbon, 50.55, oxygen 45, and hydrogen 4.45. Little reliance, however, can be placed on this result, because we are quite uncertain as to the purity of the tannin, which was combined with the lead.

From the experiments of Sir H. Davy, it appears that the inner cortical layers of barks are the richest in tannin. The quantity is greatest in the beginning of spring, at the time the buds begin to open, and smallest during winter. Of all the varieties of bark which he examined, that of the oak contains the greatest quantity of tannin.

*Artificial Tannin.*—This interesting substance was discovered twenty years ago by Mr Hatchett, who gave a full description of it in the Philosophical Transactions for 1805 and 1806. The best method of preparing it is by the action of nitric acid on charcoal. For this purpose, 100 grains of charcoal in fine powder are digested in an ounce of nitric acid, of density 1.4, diluted with two ounces of water. The mixture is exposed to a gentle heat, which is to be continued until all the charcoal is dissolved. The reddish-brown solution is then evaporated to dryness, in order to expel the pure acid, the temperature being carefully regulated towards the close of the process, so that the product may not be decomposed.

Artificial tannin is a brown fusible substance, of a resinous fracture, and astringent taste. It is soluble even in cold water and in alcohol. It reddens litmus paper, probably from adhering nitric acid. With a salt of iron and solution of gelatin, it acts precisely in the same manner as natural tannin. It differs, however, from that substance in not being decomposed by the action of strong nitric acid.

Artificial tannin may be prepared in several ways. Thus it is generated by the action of nitric acid, both on animal or vegetable charcoal, and on pit-coal. asphaltum, jet, indigo, common resin, and several resinous substances. It is also procured by treating common resin, elemi, assafœtida, camphor, balsams, &c. first with sulphuric acid, and then with alcohol.

## *Gluten. Yeast. Vegetable Albumen.*

Gluten is procured by the process which was described for preparing starch from wheat flour. (Page 468.) It has a gray colour and fibrous structure, accompanied with a high degree of viscidity and elasticity. It has scarcely any taste, and is insoluble in water, alcohol, and ether; but Dr Bostock found that a small portion is taken up by long digestion in water. Both the acids and alkalies dissolve gluten. The acid solution is precipitated by an alkali, and reciprocally the alkaline solution by an acid, the gluten in each case having lost its elasticity.

When gluten is kept in a warm moist situation it ferments, and an acid is formed; but in a few days putrefaction ensues, and an offensive odour, like that of putrefying animal matter, is emitted. According to Proust, who has made these spontaneous changes a particular object of study, the process is divisible into two distinct periods. In the first, carbonic acid and pure hydrogen gases are evolved; and in the second, besides the acetic and phosphoric acids and ammonia, two new compounds are generated, for which he proposes the names of *caseic acid* and *caseous oxide*. These are the same principles which are generated during the fermentation of the curd of milk, and their real nature will be considered in the section on milk. It is apparent from these circumstances that gluten contains nitrogen as one of its elements, and that it approaches closely to the nature of animal substances. It has hence been called a vegeto-animal principle.

If gluten is dried by a gentle heat, it contracts in volume, becomes hard and brittle, and may in this state be preserved without change. Exposed to a strong heat, it yields, in addition to the usual inflammable gases, a thick fetid oil, and carbonate of ammonia.

Gluten is present in most kinds of grain, such as wheat, barley, rye, oats, peas, and beans; but the first contains it in by far the largest proportion. This is the reason that wheaten bread is more nutritious than that made with other kinds of flour; for of all vegetable substances, gluten appears to be the most nutritive. It is to the presence of gluten that wheat flour owes its property of forming a tenacious paste with water. To the same cause is owing the formation of light spongy bread; the carbonic acid which is disengaged during the fermentation of dough, being detained by the viscid gluten, distends the whole mass, and thus produces the *rising* of the dough. From the experiments of Sir H. Davy, it appears that good wheat flour contains from 19 to 24 per cent of gluten. The wheat grown in the south of Europe is richer in gluten than that of colder climates.

M. Taddey, an Italian chemist, has succeeded in obtaining two distinct principles from gluten, to one of which he has applied the name of *gliadine*, from *γλια· gluten*, and to the other that of *zymome*, from *ζυμη*, a ferment. (Ann. of Phil. vol [illegible].)

To obtain these principles, the gluten is boiled with successive portions of alcohol, until the spirit ceases to be rendered milky by the addition of water. By this process the gliadine, which is soluble in alcohol, is dissolved, and may be procured by evaporating the alcoholic solution; while the zymome, which is insoluble in that menstruum, is left in a pure state.

Gliadine is a brittle, slightly transparent substance, of a yellow colour, and a sweetish balsamic taste. Its smell, in the cold, is like that of the honeycomb; but, when heated, it emits an odour similar to that of boiled apples. It is soluble to a considerable extent in boiling al-

cohol, and is in part deposited in cooling. The alcoholic solution is rendered milky by water, and the gliadine is precipitated in white flakes by alkaline carbonates. It is insoluble in water, but is dissolved by acids and alkalies. When heated in the open air, it takes fire, and burns with a bright flame.

Zymome is a hard tough substance, but does not possess the viscidity of gluten. It is insoluble in water and alcohol; but it is dissolved in vinegar and the mineral acids by the aid of heat, and forms a soap with pure potassa. Under favourable circumstances it putrefies, without previously fermenting like gluten; and when heated it emits an odour like that of burning hair. It produces various kinds of fermentation according to the nature of the substance with which it comes in contact.

M. Taddey has discovered a very delicate test of the presence of zymome. On mixing the powder of guaiacum with zymome, a beautiful blue colour instantly appears, and the same phenomenon ensues, though less rapidly, when it is kneaded with gluten or the flour of good wheat moistened with water. With bad flour, the gluten of which has suffered spontaneous decemposition, the blue tint is scarcely visible. The intensity of the colour, indeed, is entirely dependent on the relative quantity of zymome contained in the flour; and since the quantity of zymome is proportional to the quantity of gluten, the proportion of the latter, and therefore the quality of the flour, may be estimated approximately by the action of guaiacum.

The nature of the change which gives rise to the blue colour has not been explained; but oxygen gas is obviously essential to it, since the phenomenon does not take place at all when atmospheric air is excluded.

*Yeast.*—This substance is always generated during the vinous fermentation of vegetable juices and decoctions, rising to the surface in the form of a frothy, flocculent, somewhat viscid matter, the nature and composition of which are unknown. It is insoluble in water and alcohol, and in a warm moist atmosphere gradually putrefies, a sufficient proof that nitrogen is one of its elements. Submitted to a moderate heat, it becomes dry and hard, and may in this state be preserved without change. Heated to redness in close vessels, it yields products similar to those procured under the same circumstances from gluten. To this substance, indeed, yeast is supposed by some chemists to be very closely allied.

The most remarkable property of yeast is that of exciting fermentation. By exposure for a few minutes to the heat of boiling water, it loses this property, but after some time again acquires it. Nothing conclusive is known concerning either the nature of these changes, or the mode in which yeast operates in establishing the fermentative process.

*Vegetable Albumen.*—Some vegetables contain a substance coagulable by heat, and which is very analogous to animal albumen or curd. It was found in the bitter almond by Vogel, in the sweet almond by M. Boullay, and probably exists in most of the emulsive seeds. (Ann. of Ph. vol. xii. p. 89.)

## *Asparagin, Bassorin, Caffein, Cathartin, Fungin, Suberin, Ulmin, Lupulin, Inulin, Medullin, Pollenin, Piperin, Olivile, Sarcocoll, Rhubarbarin, Colocyntin, Bitter Principle, Extractive Matter.*

*Asparagin.*—This principle was discovered by MM. Vauquelin and Robiquet in the juice of the asparagus, from which it is deposited in crystals by evaporation. The form of its crystals is a rectangular octahedron, six-sided prism, or right rhombic prism. Its taste is cool and slightly nauseous; it is soluble in water, and has neither an acid nor alkaline reaction. (Ann. de Ch. lvii. 88.)

*Bassorin* was first noticed in gum *bassora* by Vauquelin. According to Gehlen and Bucholz, it is contained, together with common gum, in the gum tragacanth; and John found it in the gum of the cherry tree. Salep, from the experiments of Caventou, appears to consist almost totally of bassorin.

Bassorin is characterized by forming with cold water a bulky jelly, which is insoluble in that menstruum, as well as in alcohol and ether. Boiling water does not dissolve it, except by long continued ebullition, when the bassorin at length disappears, and is converted into a substance similar to gum arabic.

*Caffein* was discovered in coffee by M. Robiquet in the year 1821, and was soon after obtained from the same source by Pelletier and Caventou, without a knowledge of the discovery of Robiquet. It is a white crystalline volatile matter, which is soluble in boiling water and alcohol, and is deposited on cooling in the form of silky filaments like amianthus. M. Pelletier, contrary to the opinion of M. Robiquet, at first regarded it as an alkaline base; but he now admits that it does not affect the vegetable blue colours, nor combine with acids. (Journal de Pharmacie for May 1826.)

Hitherto the properties of caffein have not been fully described. From the analysis of Pelletier and Dumas, 100 parts of it consist of carbon 46.51, nitrogen 21.54, hydrogen 4.81, and oxygen 27.14. Though it contains more nitrogen than most animal substances, it does not, under any circumstances, undergo the putrefactive fermentation.

*Cathartin.*—This name has been applied by MM. Lassaigne and Feneulle to the active principle of senna. (An. de Ch. et de Ph. vol. xvi.)

*Fungin.*—This name is applied by M. Braconnot to the fleshy substance of the mushroom. It is procured in a pure state by digestion in hot water, to which a little alkali is added. Fungin is nutritious in a high degree, and in composition is very analogous to animal substances. Like flesh, it yields nitrogen gas when digested in dilute nitric acid.

*Suberin.*—This name has been applied by M. Chevreul to the cellular tissue of the common cork, the outer bark of the cork-oak, (*quercus suber*,) after the astringent, oily, resinous, and other soluble matters have been removed by the action of water and alcohol. Suberin differs from all other vegetable principles by yielding the suberic when treated by nitric acid.

*Ulmin,* discovered by Klaproth, is a substance which exudes spontaneously from the elm, oak, chesnut, and other trees; and according to Berzelius is a constituent of most kinds of bark. It may be prepared by acting upon elm-bark by hot alcohol, and cold water, and

then digesting the residue in water which contains an alkaline carbonate in solution. On neutralizing the alkali with an acid, the ulmin is precipitated.

Ulmin is a dark brown, nearly black substance, is insipid and inodorous, and is very sparingly soluble in water and alcohol. It dissolves freely, on the contrary, in the solution of an alkaline carbonate, and is thrown down by an acid.

*Lupulin* is the name applied by Dr Ives to the active principle of the hop, but which has not yet been obtained in a state of purity.

*Inulin* is a white powder like starch, which is spontaneously deposited from a decoction of the roots of the *Inula helenium* or *elecampane*. This substance is insoluble in cold, and soluble in hot water, and is deposited from the latter as it cools, a character which distinguishes it from starch. With iodine it forms a greenish-yellow compound of a perishable nature. Its solution is somewhat mucilaginous; but inulin is distinguished from gum by insolubility in cold water, and in not yielding the saccholactic when digested in nitric acid.

*Medullin.*—This name was applied by John to the pith of the sunflower, but its existence as an independent principle is somewhat dubious. The term *pollenin* has been given by the same chemist to the pollen of tulips.

*Piperin* is the name which is applied to a white crystalline substance extracted from black pepper. It is tasteless, and is quite free from pungency, the stimulating property of the pepper being found to reside in a fixed oil. (Pelletier, in An. de Ch. et de Ph. vol. xvi.)

*Olivile.*—When the gum of the olive tree is dissolved in alcohol, and the solution is allowed to evaporate spontaneously, a peculiar substance, apparently different from the other proximate principles hitherto examined, is deposited either in flattened needles or as a brilliant amylaceous powder. To this M. Pelletier, its discoverer, has given the name of *olivile*. (An. of Phil. vol. xii.)

*Sarcocoll* is the concrete juice of the *Penæa sarcocolla*, a plant which grows in the northern parts of Africa. It is imported in the form of small grains of a yellowish or reddish colour like gum arabic, to which its properties are similar. It has a sweetish taste, dissolves in the mouth like gum, and forms a mucilage with water. It is distinguished from gum, however, by its solubility in alcohol, and by its aqueous solution being precipitated by tannin. Dr Thomson, who has given a full account of sarcocoll in his System of Chemistry, considers it closely allied to the saccharine matter of liquorice.

*Rhubarbarin* is the name employed by Pfaff to designate the principle in which the purgative property of the rhubarb resides. M. Nani of Milan regards the active principle of this plant as a vegetable alkali; but he has not given any proof of its alkaline nature. (Journal of Science, vol. xvi. page 172.)

*Colocyntin.*—This name is applied by Vauquelin to a bitter resinous matter extracted from colocynth, and to which he ascribes the properties of this substance. (Journal of Science, vol. xviii. page 400.)

*Bitter Principle.*—This name was formerly applied to a substance supposed to be common to bitter plants, and to be the cause of their peculiar taste. The recent discoveries in vegetable chemistry, however, have shown that it can no longer be regarded as a uniform unvarying principle. The bitterness of the *nux vomica*, for example, is owing to strychnia, that of opium to morphia, that of cinchona bark to cinchonia and quinia, &c. The cause of the bitter taste in the

root of the squill is different from that of the hop or of gentian. The term bitter principle, when applied to any one principle common to bitter plants, conveys an erroneous idea, and should, therefore, be abandoned.

*Extractive Matter.*—This expression, if applied to one determinate principle supposed to be the same in different plants, is not less vague than the foregoing. It is indeed true that most plants yield to water a substance which differs from gum, sugar, or any proximate principle of vegetables, which, therefore, constitutes a part of what is called an *extract* in pharmacy, and which, for want of a more precise term, may be expressed by the name of *extractive*. It must be remembered, however, that this matter is always mixed with other proximate principles, and that there is no proof whatever of its being identical in different plants. The solution of saffron in hot water, said to afford pure extractive matter by evaporation, contains the colouring matter of the plant, together with all the other vegetable principles of saffron, which happen to be soluble in the menstruum employed.

## SECTION VI.

### *ON THE SPONTANEOUS CHANGES OF VEGETABLE MATTER.*

Vegetable substances, for reasons already explained in the remarks introductory to the study of organic chemistry, are very liable to spontaneous decomposition. So long, indeed, as they remain in connection with the living plant by which they were produced, the tendency of their elements to form new combinations is controlled; but as soon as the vital principle is extinct, of whose agency no satisfactory explanation can at present be afforded, they become subject to the unrestrained influence of chemical affinity. To the spontaneous changes which they then experience from the operation of this power, the term *fermentation* is applied.

As might be expected from the difference in the constitution of different vegetable compounds, they are not all equally prone to fermentation; nor is the nature of the change the same in all. Thus alcohol, oxalic, acetic, and benzoic acids, probably the vegetable alkalies, and pure naphtha, may be kept for years without change, and some of them appear unalterable; while others, such as gluten, sugar, starch, and mucilaginous substances, are very liable to decomposition. In like manner, the spontaneous change sometimes terminates in the formation of sugar, at another time in that of alcohol, at a third in that of acetic acid, and at a fourth in the total dissolution of the substance. This has led to the division of the fermentative processes into four distinct kinds, namely, the *saccharine*, the *vinous*, the *acetous*, and the *putrefactive* fermentation.

### *Saccharine Fermentation.*

The only substance known to be subject to the first kind of fermentation is starch. When gelatinous starch, or amidine, is kept in a moist state for a considerable length of time, a change gradually ensues, and a quantity of sugar, equal to about half the weight of the

starch employed, is generated. Exposure to the atmosphere is not necessary to this change, but the quantity of sugar is increased by the access of air.

The germination of seeds, as exemplified in the malting of barley, is likewise an instance of the saccharine fermentation; but as it differs in some respects from the process above mentioned, being probably modified by the vitality of the germ, it may with greater propriety be discussed in the following section.

The ripening of fruit has also been regarded as an example of the saccharine fermentation, especially since some fruits, such as the pear and apple, if gathered before their maturity, become sweeter by keeping. I cannot, however, adopt this opinion. The process of ripening appears to consist in the conversion, not of starch, but of acid into sugar. Such at least is the view deducible from the experiments of Proust, who examined the unripe grape in its different stages towards maturity. He found that the green fruit contains a large quantity of free acid, chiefly the citric, which gradually disappears as the grape ripens, while its place is occupied by sugar. It is hence probable that the elements of the acid itself, as the result of a vital process, are made to enter into a new arrangement, by which sugar is generated. The formation of an acid may be regarded as one step towards the production of saccharine matter, a view which will account for the strong acidity of many fruits, such as the gooseberry and currant, just before they begin to ripen.

## *Vinous Fermentation.*

The conditions which are required for establishing the vinous fermentation are four in number; namely, the presence of sugar, water, yeast, or some ferment, and a certain temperature. The best mode of studying this process, so as to observe the phenomena, and determine the nature of the change, is to place five parts of sugar, with about twenty of water, in a glass flask furnished with a bent tube, the extremity of which opens under an inverted jar full of water or mercury; and after adding a little yeast, to expose the mixture to a temperature of about 60° or 70° Fahr. In a short time bubbles of gas begin to collect in the vicinity of the yeast, and the liquid is soon put into brisk motion, in consequence of the formation and disengagement of a large quantity of gaseous matter; the solution becomes turbid, its temperature rises, and froth collects upon its surface. After continuing for a few days, the evolution of gas begins to abate, and at length ceases altogether; the impurities gradually subside, and leave the liquor clear and transparent.

The only appreciable changes which are found to have occurred during the process, are the disappearance of the sugar, and the formation of alcohol, which remains in the flask, and of carbonic acid gas, which is collected in the pneumatic apparatus. A small portion of yeast is indeed decomposed; but the quantity is so minute that it may without inconvenience be left out of consideration. The yeast indeed appears to operate only in exciting the fermentation, without further contributing to the products. The atmospheric air, it is obvious, has no share in the phenomena, since it may be altogether excluded without affecting the result. The theory of the process is founded on the fact that the sugar, which disappears, is almost precisely equal to the united weights of the alcohol and carbonic acid; and hence the former is supposed to be resolved into the two latter. in which this change is conceived to take place has been

ably explained by Gay-Lussac, an explanation which will easily be understood by comparing the composition of sugar with that of alcohol. The elements of sugar, which consists of carbon, hydrogen, and oxygen, in the ratio of one equivalent of each, (page 467) are multiplied by three, in order to equalize the quantity of hydrogen contained in the two compounds. (An. de Ch. tome xcv. p. 317.)

*By weight.*

| | *Sugar.* | *Alcohol.* |
|---|---|---|
| Carbon, . | 18 or three equivalents. | 12 or two equivalents. |
| Hydrogen, . | 3 or three equivalents. | 3 or three equivalents. |
| Oxygen, . | 24 or three equivalents. | 8 or one equivalent. |
| | — 45 | — 23 |

*By volume.*

| | *Sugar.* | *Alcohol.* |
|---|---|---|
| Vap. of Carbon, | 3 | 2 |
| Hydrogen, . | 3 | 3 |
| Oxygen, . | $1\frac{1}{2}$ | $\frac{1}{2}$ |

Now, on inspecting this table, and remembering that carbonic acid consists of one equivalent of carbon, or one volume of its vapour, and two equivalents or one volume of oxygen, it will be apparent that the elements of sugar are in such proportion as to form one equivalent of alcohol, or one volume of its vapour, and one equivalent or one volume of carbonic acid. Therefore forty-five parts of sugar are capable of furnishing twenty-three parts of alcohol, and twenty-two parts of carbonic acid.

It admits of doubt whether any substance besides sugar is capable of undergoing the vinous fermentation. The only other principle which is supposed to possess this property is starch, and this opinion chiefly rests on the two following facts. First, it is well known that potatoes, which contain but little sugar, yield a large quantity of alcohol by fermentation, during which the starch disappears. And, secondly, M. Clement procured the same quantity of alcohol from equal weights of malted and unmalted barley.* Nothing conclusive can be inferred, however, from these data; for, from the facility with which starch is converted into sugar, it is probable that the saccharine may precede the vinous fermentation.

Though a solution of pure sugar is not susceptible of the vinous fermentation without being mixed with yeast, or some such ferment, yet the saccharine juices of plants do not require the addition of that substance, or, in other words, they contain some principle which, like yeast, excites the fermentative process. Thus, must or the juice of the grape ferments spontaneously; but Gay-Lussac has observed that these juices cannot begin to ferment unless they are exposed to the air. By heating must to 212° F, and then corking it carefully, the juice may be preserved without change; but if it be exposed to the air for a few seconds only, it absorbs oxygen, and fermentation takes place. From this it would appear that the must contains a principle which is convertible into yeast, or at least acquires the characteristic property of that substance by absorbing oxygen.

It appears from the experiments of M. Colin, that various substances are capable of acting as a ferment. This property is possessed by gluten, as well as both its principles, gliadine and zymome, caseous

* Annales de Chimie et de Physique, tome v. p. 422.

matter, albumen, fibrin, gelatin, blood, and urine. In general they act most efficaciously after the commencement of putrefaction; and indeed exposure to oxygen gas seems equally necessary for enabling these substances to act as ferments, as to the principle contained in the juice of fruit.

The various kinds of stimulating fluids, prepared by means of the vinous fermentation, are divisible into wines which are formed from the juices of saccharine fruits, and the various kinds of ale and beer produced from a decoction of the nutritive grains previously malted.

The juice of the grape is superior, for the purpose of making wine, to that of all other fruits, not merely in containing a larger proportion of saccharine matter, since this deficiency may be supplied artificially, but in the nature of its acid. The chief or only acidulous principle of the mature grape, ripened in a warm climate, such as Spain, Portugal, or Madeira, is the bitartrate of potassa. As this salt is insoluble in alcohol, the greater part of it is deposited during the vinous fermentation; and an additional quantity subsides, constituting the *crust*, during the progress of wine towards its point of highest perfection. The juices of other fruits, on the contrary, such as the gooseberry or currant, contain the malic and citric acids, which are soluble both in water and alcohol, and of which therefore they can never be deprived. Consequently these wines are only rendered palatable by the presence of free sugar, which conceals the taste of the acid; and hence it is necessary to arrest the progress of the fermentation long before the whole of the saccharine matter is consumed. For the same reason, these wines do not admit of being long kept; for as soon as the free sugar is converted into alcohol by the slow fermentative process, which may be retarded by the addition of brandy, but cannot be prevented, the wine acquires a strong sour taste.

Ale and beer differ from wines in containing a large quantity of mucilaginous and extractive matters derived from the malt with which they are made. From the presence of these substances they always contain a free acid, and are greatly disposed to pass into the acetous fermentation. The sour taste is concealed partly by free sugar, and partly by the bitter flavour of the hop, the presence of which diminishes the tendency to the formation of an acid.

The fermentative process which takes place in dough mixed with yeast, and on which depends the formation of good bread, has been supposed to be of a peculiar kind, and is sometimes designated by the name of *panary fermentation*. The late ingenious researches of Dr Colquhoun, however, leave little or no doubt that the phenomena are to be ascribed to the saccharine matter of the flour undergoing the vinous fermentation, by which it is resolved into alcohol and carbonic acid. (Edinburgh Journal of Science, vol. vi.) Indeed Mr Graham has actually procured alcohol by distillation from fermented dough.

## *Acetous Fermentation.*

When any liquid which has undergone the vinous fermentation, or even pure alcohol diluted with water, is mixed with yeast, and exposed in a warm place to the open air, an intestine movement speedily commences, heat is developed, the fluid becomes turbid from the deposition of a peculiar filamentous matter, oxygen is absorbed from the atmosphere, and carbonic acid is disengaged. These changes, after continuing a certain time, cease spontaneously; the liquor becomes clear, and instead of alcohol, it is now found to contain acetic acid. This process is called the *acetous fermentation*.

The vinous may easily be made to terminate in the acetous fermentation; nay, the transition takes place so easily, that in many instances, in which it is important to prevent it, this is with difficulty effected. It is the uniform result, if the fermenting liquid be exposed to a warm temperature and to the open air; and the means by which it is avoided is by excluding the atmosphere, or by exposure to cold.

For the acetous fermentation a certain degree of warmth is indispensable. It takes place tardily below 60° F.; at 50° it is very sluggish; and at 32°, or not quite so low, it is wholly arrested. It proceeds with vigour, on the contrary, when the thermometer ranges between 60° and 80°, and is even promoted by a temperature somewhat higher. The presence of water is likewise essential; and a portion of yeast, or some analogous substance, by which the process may be established, must also be present.

The information contained in chemical works relative to the substances susceptible of the acetous fermentation is somewhat confused, a circumstance which appears to have arisen from phenomena of a totally different nature being included under the same name. It seems necessary to distinguish between the mere formation of acetic acid, and the acetous fermentation. Several or perhaps most vegetable substances yield acetic acid when they undergo spontaneous decomposition. Mucilaginous substances in particular, though excluded from the air, gradually become sour; and consistently with this fact, inferior kinds of ale and beer are known to acquire acidity in a short time, even when confined in well-corked bottles. In like manner, a solution of sugar, mixed with water in which the gluten of wheat has fermented, and kept in close vessels, was found by Fourcroy and Vauquelin to yield acetic acid. All these processes, however, appear essentially different from the proper acetous fermentation above described, being unattended with visible movement in the liquid, with absorption of oxygen, or disengagement of carbonic acid.

The acetous fermentation, in this limited sense, consists in the conversion of alcohol into acetic acid. That this change does really take place is inferred, not only from the disappearance of alcohol and the simultaneous production of acetic acid, but also from the quantity of the latter being precisely proportional to that of the former. The nature of the chemical action, however, is at present exceedingly obscure. Indeed the only probable explanation which has been offered is the following. Since alcohol contains a greater proportional quantity of carbon and hydrogen than acetic acid, it has been supposed that the oxygen of the atmosphere, the presence of which is indispensable, abstracts so much of those elements, by giving rise to the formation of carbonic acid and water, as to leave the remaining carbon, hydrogen, and oxygen of the alcohol in the precise ratio for forming acetic acid. The experiments of Saussure, however, are incompatible with this view. According to his researches, the quantity of carbonic acid generated during the acetous fermentation is precisely equal in volume to the oxygen which is absorbed; and hence it is inferred, that this gas unites exclusively with the carbon of the alcohol. This result is different from what might have been anticipated, and requires confirmation.

The acetous fermentation is conducted on a large scale for yielding the common vinegar of commerce. In France it is prepared by exposing weak wines to the air during warm weather; and in this country it is made from a solution of brown sugar or molasses, or an infusion of malt. The vinegar thus obtained always contains a large quantity

of mucilaginous and other vegetable matters, the presence of which renders it liable to several ulterior changes.

## *Putrefactive Fermentation.*

By this term is implied a process which is not attended with the phenomena of the saccharine, vinous, or acetous fermentation, but during which the vegetable matter is completely decomposed. All proximate principles are not equally liable to this kind of dissolution. Those in which charcoal and hydrogen prevail, such as the oils, resins, and alcohol, do not undergo the putrefactive fermentation; nor do acids, which contain a considerable excess of oxygen, manifest a tendency to suffer this change. Those substances are alone disposed to putrefy, the oxygen and hydrogen of which are in proportion to form water; and such, in particular, as contain nitrogen. Among these, however, a singular difference is observable. Caffein evinces no tendency to spontaneous decomposition; while gluten, which certainly must contain a less proportional quantity of nitrogen, putrefies with great facility. It is difficult to assign the precise cause of this difference; but it most probably depends partly upon the mode in which the ultimate elements of bodies are arranged, and partly on their cohesive power;—those substances, the texture of which is the most loose and soft, being, *cæteris paribus*, the most liable to spontaneous decomposition.

The conditions which are required for enabling the putrefactive process to take place, are moisture, air, and a certain temperature.

The presence of a certain degree of moisture is absolutely necessary; and hence vegetable substances, which are disposed to putrefy under favourable circumstances, may be preserved for an indefinite period if carefully dried, and protected from humidity. Water acts apparently by softening the texture, and thus counteracting the agency of cohesion; and a part of the effect may also be owing to its affinity for some of the products of the putrefaction. It is not likely that this liquid is actually decomposed, since water appears to be a uniform product.

The air cannot be regarded as absolutely necessary, since putrefaction is found to be produced by the concurrence of the two other conditions only; but the process is without doubt materially promoted by free exposure to the atmosphere. Its operation is of course attributable to the oxygen combining with the carbon and hydrogen of the decaying substance.

The temperature most favourable to the putrefactive process is between 60° and 100° Fahr. A strong heat is unfavourable, by expelling moisture; and a cold of 32° F. at which water congeals, arrests its progress altogether. The mode in which caloric acts is the same as in all similar cases, namely, by tending to separate elements from one another which are already combined.

The products of the putrefactive fermentation may be divided into the solid, liquid, and gaseous. The liquid are chiefly water, together with a little acetic acid, and probably oil. The gaseous products are light carburetted hydrogen, carbonic acid, and, when nitrogen is present, ammonia. Pure hydrogen, and probably nitrogen, are sometimes disengaged. Thus hydrogen and carbonic acid, according to Proust, are evolved from putrefying gluten; and Saussure obtained the same gases from the putrefaction of wood in close vessels. Under ordinary circumstances, however, the chief gaseous product of decaying plants is light carburetted hydrogen, which is generated in great quantity at the bottom of stagnant pools during summer and autumn. (Page 191.)

Another elastic principle, supposed to arise from putrefying vegetable remains, is the noxious miasm of marshes. The origin of these miasms, however, is exceedingly obscure. Every attempt to obtain them in an insulated state has hitherto proved abortive; and, therefore, if they are really a distinct species of matter, they must be regarded, like the effluvia of contagious fevers, as of too subtile a nature for being subjected to chemical analysis.

When the decay of leaves or other parts of plants has proceeded so far that all trace of organization is effaced, a dark pulverulent substance remains, consisting of charcoal combined with a little oxygen and hydrogen. This compound is vegetable mould, which, when mixed with a proper quantity of earth, constitutes the soil necessary to the growth of plants. Saussure, in his excellent *Recherches Chimiques sur la Vegetation*, has described vegetable mould as a substance of uniform composition; and on heating it to redness in close vessels, he procured carburetted hydrogen and carbonic acid gases, water holding the acetate or carbonate of ammonia in solution, a minute quantity of empyreumatic oil, and a large residue of charcoal mixed with saline and earthy ingredients. On exposing vegetable mould to the action of light, air, and moisture, a chemical change ensues, the effect of which is to render a portion of it soluble in water, and thus applicable to the nutrition and growth of plants.

## SECTION VII.

### *ON THE CHEMICAL PHENOMENA OF GERMINATION AND VEGETATION.*

### *Germination.*

Germination is the process by which a new plant originates from seed. A seed consists essentially of two parts, the *germ* of the future plant, endowed with a principle of vitality, and the *cotyledons* or *seed-lobes*, both of which are enveloped in a common covering of cuticle. In the germ, two parts, the *radicle* and *plumula*, may be distinguished, the former of which is destined to descend into the earth and constitute the root, the latter to rise into the air and form the stem of the plant. The office of the seed-lobes is to afford nourishment to the young plant, until its organization is so far advanced, that it may draw materials for its growth from extraneous sources. For this reason, seeds are composed of highly nutritious ingredients. The chief constituent of most of them is starch, in addition to which they frequently contain gluten, gum, vegetable albumen or curd, and sugar.

The conditions necessary to germination are three-fold; namely, moisture, a certain temperature, and the presence of oxygen gas. The necessity of moisture to this process has been proved by extensive observation. It is well known that the concurrence of other conditions cannot enable the seeds to germinate provided they are kept quite dry.

A certain degree of warmth is not less essential than moisture. Germination cannot take place at 32° F; and a strong heat, such as that of boiling water, prevents it altogether by depriving the germ of the vital principle. The most favourable temperature ranges from 60° to 80°, the precise degree varying with the nature of the plant, a circum-

stance that accounts for the difference in the season of the year at which different seeds begin to germinate.

That the presence of air is necessary to germination was demonstrated by several philosophers, such as Ray, Boyle, Muschenbroeck, and Boerhaave, before the chemical nature of the atmosphere was discovered; and Scheele, soon after the discovery of oxygen, proved that beans do not germinate without exposure to that gas. Achard afterwards demonstrated the same fact with respect to seeds in general, and his experiments have been fully confirmed by subsequent observers. It has even been shown by Humboldt, that a dilute solution of chlorine, owing to the tendency of that gas to decompose water and set oxygen at liberty, promotes the germination of seeds. These circumstances account for the fact that seeds, when buried deep in the earth, are unable to germinate.

It is remarkable that the influence of light, which is so favourable to all the subsequent stages of vegetation, is injurious to the process of germination. Ingenhousz and Sennebier have proved that a seed germinates more rapidly in the shade than in light, and in diffused daylight quicker than when exposed to the direct solar rays.

From the preceding remarks it is apparent that when a seed is placed an inch or two under the surface of the ground in spring, and is loosely covered with earth, it is in a state every way conducive to germination. The ground is warmed by absorbing the solar rays, and is moistened by occasional showers; the earth at the same time protects the seed from light, but by its porosity gives free access to the air.

The operation of malting barley, in which the grain is made to germinate by exposure to warmth, air, and humidity, affords the best means of studying the phenomena of germination. In this process, water is absorbed, the cotyledon swells and ruptures its cuticle, and soon after the radicle and plumula are protruded. On examining the grain at this period, it is found to have undergone an essential change in the proportion of its ingredients, as appears from the result of Proust's comparative analysis of malted and unmalted barley. (An de Ch. et de Ph. tome v.)

| | *In* 100 *parts of Barley.* | *In* 100 *parts of Malt.* |
|---|---|---|
| Resin, | 1 | 1 |
| Gum, | 4 | 15 |
| Sugar, | 5 | 15 |
| Gluten, | 3 | 1 |
| Starch, | 32 | 56 |
| Hordein | 55 | 12 |

It is hence apparent that in germination, the hordein is converted into starch, gum, and sugar; so that from an insoluble material, which could not in that state be applied to the uses of the young plant, two soluble and highly nutritive principles result, which by being dissolved in water are readily absorbed by the radicle.

The chemical changes which take place in germination have been ably investigated by Saussure, whose experiments are detailed in the work to which I have already referred. The leading facts which he determined are the following;—that oxygen gas is consumed, that carbonic acid is evolved, and that the volume of the latter is precisely equal to that of the former. Now since carbonic acid gas contains its own volume of oxygen, it follows that this gas must have united exclusively with carbon. It is likewise obvious that the grain must weigh less

after than before germination, provided it is brought to the same state of dryness in both instances. Saussure indeed found that the loss is greater than can be accounted for by the carbon of the carbonic acid which is evolved, and hence he concluded that a portion of water, generated at the expense of the grain itself, is dissipated in drying. According to Proust, the diminution in weight is about a third; but Dr Thomson affirms that in 50 processes, conducted on a large scale under his inspection, the average loss did not exceed one-fifth.

## *On the Growth of Plants.*

While a plant differs from an animal in exhibiting no signs of perception or voluntary motion, and in possessing no stomach to serve as a receptacle for its food, there exists between them a close analogy both of parts and functions, which, though not discerned at first, becomes striking on a near examination. The stem and branches act as a frame-work or skeleton for the support and protection of the parts necessary to the life of the individual. The root serves the purpose of a stomach by imbibing nutritious juices from the soil, and thus supplying the plant with materials for its growth. The sap or circulating fluid, composed of water holding in solution, saline, extractive, mucilaginous, saccharine, and other soluble substances, rises upwards through the wood in a distinct system of tubes called the *common vessels*, which correspond in their office to the lacteals and pulmonary arteries of animals, and are distributed in minute ramifications over the surface of the leaves. In its passage through this organ, which may be termed the lungs of a plant, the sap is fully exposed to the agency of light and air, experiences a change by which it is more completely adapted to the wants of the vegetable economy, and then descends through the inner layer of the bark in another system of tubes called the *proper vessels*, yielding in its course all the juices and principles peculiar to the plant.

The chemical changes which take place during the circulation of the sap are in general of such a complicated nature, and so much under the control of the vital principle, as to elude the sagacity of the chemist. One part of the subject, however, namely, the reciprocal agency of the atmosphere and growing vegetables on each other, falls within the reach of chemical inquiry, and has accordingly been investigated by several philosophers.

For the leading facts relative to what is called the *respiration* of plants, or the chemical changes which the leaves of growing vegetables produce on the atmosphere, we are indebted to Priestley and Ingenhousz, the former of whom discovered that plants absorb carbonic acid from the air, under certain circumstances, and emit oxygen in return; and the latter ascertained that this change occurs only during exposure to the direct rays of the sun. When a healthy plant, the roots of which are supplied with proper nourishment, is exposed to the direct solar beams in a given quantity of atmospheric air, the carbonic acid after a certain interval is removed, and an equal volume of oxygen is substituted for it. If a fresh portion of carbonic acid is supplied, the same result will ensue. In like manner, Sennebier and Woodhouse observed, that when the leaves of a plant are immersed in water, and exposed to the rays of the sun, oxygen gas is disengaged. That the evolution of oxygen in this experiment is accompanied with a proportional absorption of carbonic acid, is proved by employing water deprived of carbonic acid by boiling, in which case no oxygen is procured.

Such are the changes induced by plants when exposed to sunshine; but in the dark an opposite effect ensues. Carbonic acid gas is not absorbed under these circumstances, nor is oxygen gas evolved; but, on the contrary, oxygen disappears, and carbonic acid gas is disengaged. In the dark, therefore, vegetables deteriorate rather than purify the air, producing the same effect as the respiration of animals.

From several of the preceding facts, it is supposed that the oxygen emitted by plants while under the influence of light is derived from the carbonic acid which they absorb, and that the carbon of that gas is applied to the purposes of nutrition. Consistently with this view it has been observed that plants do not thrive when kept in an atmosphere of pure oxygen; and it was found by Dr Percival and Mr Henry, that the presence of a little carbonic acid is even favourable to their growth. Saussure, who examined this subject minutely, ascertained that plants grow better in an atmosphere which contains about one-twelfth of carbonic acid, than in common air, provided they are exposed to sunshine; but if that gas be present in a greater proportion, its influence is prejudicial. In an atmosphere consisting of one-half of its volume of carbonic acid, the plants perished in seven days; and they did not vegetate at all when that gas was in the proportion of two-thirds. In the shade, the presence of carbonic acid is always detrimental. He likewise observed that the presence of oxygen is necessary, in order that a plant should derive benefit from admixture with carbonic acid.

Saussure is of opinion that plants derive a large quantity of their carbon from the carbonic acid of the atmosphere, an opinion which receives great weight from the two following comparative experiments. On causing a plant to vegetate in pure water, supplied with common air and exposed to light, the carbon of the plant increased in quantity; but when supplied with common air, in a dark situation, it even lost a portion of the carbon which it had previously possessed.

Light is necessary to the colour of plants. The experiments of Sennebier and Mr Gough have shown that the green colour of the leaves is not developed, except when they are in a situation to absorb oxygen and give out carbonic acid.

Though the experiments of different philosophers agree as to the influence of vegetation on the air in sunshine and during the night, considerable uncertainty prevails both as to the phenomena occasioned by diffused daylight, and concerning the total effect produced by plants on the constitution of the atmosphere. Priestley found that air, vitiated by combustion or the respiration of animals, and left in contact for several days and nights with a sprig of mint, was gradually restored to its original purity; and hence he inferred that the oxygen gas consumed during these and various other processes, is restored to the mass of the atmosphere by the agency of growing vegetables.

This doctrine receives confirmation from the researches of Ingenhousz and Saussure, who were led to adopt the opinion that the quantity of oxygen gas evolved from plants by day, exceeds that of carbonic acid emitted during the night. The conclusions of Mr Ellis, on the contrary, are precisely the reverse. From an extensive series of experiments, contrived with much sagacity, Mr Ellis inferred that growing plants give out oxygen only in direct sunshine, while at all other times they absorb it; that when exposed to the ordinary vicissitudes of sunshine and shade, light and darkness, they form more carbonic acid in the period of a day and night, than they destroy; and, consequently, that the general effect of vegetation on the atmosphere is the same as

that produced by animals. (Ellis's Researches and Farther Inquiries on Vegetation, &c.)

This question has been ably discussed by Sir H. Davy, in his Elements of Agricultural Chemistry. Sir H. Davy is of opinion that the experiments of Mr Ellis cannot be regarded as decisive, having been conducted under circumstances unfavourable to accuracy of result. He considers the original experiments of Priestley as unexceptionable, and adduces others made by himself in support of the same doctrine.

## *On the Food of Plants.*

The chief source from which plants derive the materials for their growth is the soil. However various the composition of the soil, it consists essentially of two parts, so far as its solid constituents are concerned. One is a certain quantity of earthy matters, such as siliceous earth, clay, lime, and sometimes magnesia; and the other is formed from the remains of animal and vegetable substances, which, when mixed with the former, constitute common mould. A mixture of this kind, moistened by rain, affords the proper nourishment of plants. The water, percolating through the mould, dissolves the soluble salts with which it comes in contact, together with the gaseous, extractive, and other matters, which are formed during the decomposition of the animal and vegetable remains. In this state it is readily absorbed by the roots, and conveyed as sap to the leaves, where it undergoes a process of assimilation.

But though this is the natural process by which plants obtain the greater part of their nourishment, and without which they do not arrive at perfect maturity, they may live, grow, and even increase in weight, when wholly deprived of nutrition from this source. Thus in the experiment of Saussure, already described, sprigs of peppermint were found to vegetate in distilled water; and it is well known that many plants grow when merely suspended in the air. In the hot-houses of the botanical garden of Edinburgh, for example, there are two plants, species of the fig-tree, the *Ficus australis* and *Ficus elastica*, the latter of which, as Dr Graham informs me, has been suspended for four, and the former for nearly ten years, during which time they have continued to send out shoots and leaves.

Before scientific men had learned to appreciate the influence of atmospheric air on vegetation, the increase of carbonaceous matter, which occurs in some of these instances, was supposed to be derived from water, an opinion naturally suggested by the important offices performed by this fluid in the vegetable economy. Without water, plants speedily wither and die. It gives the soft parts that degree of succulence necessary for the performance of their functions;—it affords two elements, oxygen and hydrogen, which either as water, or under some other form, are contained in all vegetable products;—and, lastly, the roots absorb from the soil those substances only, which are dissolved or suspended in water. So carefully, indeed, has nature provided against the chance of deficient moisture, that the leaves are endowed with a property both of absorbing aqueous vapour directly from the atmosphere, and of lowering their temperature during the night by radiation, so as to cause a deposition of dew upon their surface, in consequence of which, during the dryest seasons and in the warmest climates, they frequently continue to convey this fluid to the plant, when it can no longer be obtained in sufficient quantity from the soil. But necessary as is this fluid to vegetable life, it cannot yield to plants a principle which it does not possess. The carbonace-

ous matter which accumulates in plants, under the circumstances above mentioned, may, with every appearance of justice, be referred to the atmosphere; since we know that carbonic acid exists there, and that growing vegetables have the property of taking carbon from that gas.

When plants are incinerated, their ashes are found to contain saline and earthy matters, the elements of which, if not the compounds themselves, are supposed to be derived from the soil. Such at least is the view deducible from the researches of Saussure, and which might have been anticipated by reasoning on chemical principles. The experiments of M. Schrader, however, lead to a different conclusion. He sowed several kinds of grain, such as barley, wheat, rye, and oats, in pure flowers of sulphur, and supplied the shoots as they grew, with nothing but air, light, and distilled water. On incinerating the plants, thus treated, they yielded a greater quantity of saline and earthy matters than were originally present in the seeds.

These results, supposing them accurate, may be accounted for in two ways. It may be supposed, in the first place, that the foreign matters were introduced accidentally from extraneous sources, as by fine particles of dust floating in the atmosphere; or, secondly, it may be conceived, that they were derived from the sulphur, air, and water, with which the plants were supplied. If the latter opinion be adopted, we must infer either that the vital principle, which certainly controls chemical affinity in a surprising manner, and directs this power in the production of new compounds from elementary bodies, may likewise convert one element into another; or that some of the substances, supposed by chemists to be simple, such as oxygen and hydrogen, are compounds, not of two, but of a variety of different principles. As these conjectures are without foundation, and are utterly at variance with the facts and principles of the science, I do not hesitate in adopting the more probable opinion, that the experiments of M. Schrader were influenced by some source of error which escaped detection.

# ANIMAL CHEMISTRY.

All distinct compounds, which are derived from the bodies of animals, are called *proximate animal principles*. They are distinguished from inorganic matter by the characters stated in the introduction to organic chemistry. The circumstances which serve to distinguish them from vegetable matter are, the presence of nitrogen, their strong tendency to putrefy, and the highly offensive products to which their spontaneous decomposition gives rise. It should be remembered, however, that nitrogen is likewise a constituent of many vegetable substances; though few of these, the vegeto-animal principles excepted, (page 477), are prone to suffer the putrefactive fermentation. It is likewise remarkable that some compounds of animal origin, such as cholesterine and the oils, do not contain nitrogen as one of their elements, and are not disposed to putrefy.

The essential constituents of animal compounds are carbon, hydrogen, oxygen, and nitrogen, besides which some of them contain phosphorus, sulphur, iron, and earthy and saline matters in small quantity. Owing to the presence of sulphur and phosphorus, the process of putrefaction, which will be particularly described hereafter, is frequently attended with the disengagement of sulphuretted and phosphuretted hydrogen gases. When heated in close vessels, they yield water, carbonic oxide, carburetted hydrogen, probably free nitrogen and hydrogen, the carbonate and hydrocyanate of ammonia, and a peculiarly fetid thick oil. The carbonaceous matter left in the retort is less easily burned, and is more effectual as a decolorizing agent than charcoal derived from vegetable matter.

The principle of the method of analyzing animal substances has already been mentioned. (Page 425.)

In describing the proximate animal principles, the number of which is far less considerable than the vegetable compounds, I shall adopt the arrangement suggested by Gay-Lussac and Thenard in their *Recherches Physico-Chimiques*, and followed by Thenard in his System of Chemistry. The animal compounds are accordingly arranged in three sections. The first contains substances which are neither acid nor oleaginous; the second comprehends the animal acids; and the third includes the animal fats. Several of the principles belonging to the first division, such as fibrin, albumen, gelatin, caseous matter, and urea, were shown by Gay-Lussac and Thenard to have several points of similarity in their composition. They all contain, for example, a large quantity of carbon, and their hydrogen is in such proportion as to convert all their oxygen into water, and their nitrogen into ammonia. No general laws have been established relative to the constitution of the compounds comprised in the other sections.

## SECTION I.

### *SUBSTANCES WHICH ARE NEITHER ACID NOR OLEAGINOUS.*

### *Fibrin.*

Fibrin enters largely into the composition of the blood, and is the basis of the muscles; it may be regarded, therefore, as one of the most abundant of the animal principles. It is most conveniently procured by stirring recently drawn blood with a stick during its coagulation, and then washing the adhering fibres with water until they are perfectly white. It may also be obtained by removing the soluble parts from lean beef, cut into small slices, by digestion in several successive portions of water.

Fibrin is solid, white, insipid, and inodorous. When moist it is somewhat elastic, but on drying, it becomes hard, brittle, and semi-transparent. In a moist, warm situation, it readily putrefies. It is insoluble in water at common temperatures, and is dissolved in very minute quantity by the continued action of boiling water. Alcohol, of specific gravity 0.81, converts it into a fatty adipocirous matter, which is soluble in alcohol and ether, but is precipitated by water.

The action of acids on fibrin has been particularly described by Berzelius.* Digested in concentrated acetic acid, fibrin swells and becomes a bulky tremulous jelly, which dissolves completely, with disengagement of a little nitrogen, in a considerable quantity of hot water.

By the action of nitric acid, of specific gravity 1.25, aided by heat on fibrin, a yellow solution is formed, with disengagement of a large quantity of nearly pure nitrogen, in which Berzelius could not detect the least trace of the deutoxide of nitrogen. After digestion for twenty-four hours, a pale yellow pulverulent substance is deposited, which Fourcroy and Vauquelin described as a new acid under the name of *yellow acid.* According to Berzelius, however, it is a compound of modified fibrin and nitric acid, together with some malic and nitrous acids. It likewise contains some fatty matter, which may be removed by alcohol. The origin of the nitrogen which is disengaged in the beginning of the process, is somewhat obscure. From the total absence of the deutoxide of nitrogen, it is probable that, in the early stages, very little, if any, of the nitric acid is decomposed, and that the nitrogen gas is solely or chiefly derived from the fibrin.

Dilute muriatic acid hardens without dissolving fibrin, and the strong acid decomposes it. The action of sulphuric acid, according to M. Braconnot, is very peculiar. When fibrin is mixed with its own weight of concentrated sulphuric acid, a perfect solution ensues without change of colour, or disengagement of sulphurous acid. On diluting with water, boiling for nine hours, and separating the acid by means of chalk, the filtered solution was found to contain a peculiar white matter, to which M. Braconnot has applied the name of *leucine.* (An. de Ch. et de Ph. vol. xiii.) Digested in strong sulphuric acid, a dark

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* Medico-Chirurgical Transactions, vol. iii. p. 201, et seq.

reddish-brown, nearly black solution is formed, and the fibrin is carbonized and decomposed.

Fibrin is dissolved by pure potassa, and is thrown down when the solution is neutralized. The fibrin thus precipitated, however, is partially changed, since it is no longer soluble in acetic acid. It is soluble likewise in ammonia.

According to the analysis of Gay-Lussac and Thenard, 100 parts of fibrin are composed of carbon, 53.36, hydrogen 7.021, oxygen 19.685, and nitrogen 19.934. From these numbers, fibrin may be regarded as an atomic compound of eighteen equivalents of carbon, fourteen of hydrogen, five of oxygen, and three of nitrogen.

## *Albumen.*

Albumen enters largely into the composition both of animal fluids and solids. Dissolved in water, it forms an essential constituent of the serum of the blood, the liquor of the serous cavities, and the fluid of dropsy; and in a solid state, it is contained in several of the textures of the body, such as the cellular membrane, the skin, glands, and vessels. From this it appears that albumen exists under two forms, liquid and solid.

Liquid albumen is best procured from the white of eggs, which consists almost solely of this principle, united with water and free soda, and mixed with a small quantity of saline matter. In this state, it is a thick glairy fluid, insipid, inodorous, and easily miscible with cold water, in a sufficient quantity of which it is completely dissolved. When exposed in thin layers to a current of air it dries, and becomes a solid and transparent substance, which retains its solubility in water, and may be preserved for any length of time without change. Kept in its fluid condition, it readily putrefies. From the free soda which they contain, albuminous liquids have always an alkaline reaction.

Liquid albumen is coagulated by heat, alcohol, and the stronger acids. Undiluted albumen is coagulated by a temperature of 160°, and when diluted with water, at 212° F. Water which contains only 1-1000th of its weight of albumen is rendered opake by boiling. (Bostock.) On this property is founded the method of clarifying by means of albuminous solutions; for the albumen being coagulated by heat, entangles in its substance all the foreign particles which are not actually dissolved, and carries them with it to the surface of the liquid. The character of being coagulated by hot water distinguishes albumen from all other animal fluids.

The acids differ in their action on albumen. The sulphuric, muriatic, and nitric acids coagulate it; and in each case, according to Thenard, some of the acid is retained by the albumen. Phosphoric acid, recently ignited, likewise coagulates albumen; but on keeping the acid dissolved in water, its power of producing coagulation gradually declines, and after a few days ceases altogether. The solution of albumen is not precipitated at all by acetic acid. By maceration in dilute nitric acid for a month, it is converted, according to Mr Hatchett, into a substance soluble in hot water, and possessed of the leading properties of gelatin. Digested in strong sulphuric acid, the coagulum is dissolved, and a dark solution is formed similar to that produced by the same acid on fibrin; but if the heat be applied very cautiously, the liquid assumes a beautiful red colour. This property was discovered some years ago by Dr Hope, who informs me that the experimen does not always succeed, the result being influenced by very sligh causes.

Albumen is precipitated by several reagents, especially by metallic salts. This effect is produced by muriate of tin, subacetate of lead, muriate of gold, and solution of tannin. Corrosive sublimate is a very delicate test of the presence of albumen, causing a milkiness when the albumen is diluted with 2000 parts of water. The nature of the precipitate has already been explained. (Page 359.) The ferrocyanate of potassa is equally if not still more delicate, provided a little acetic acid is previously added to neutralize the free soda.

When an albuminous liquid is exposed to the agency of galvanism, pure soda makes its appearance at the negative wire, and the albumen coagulates around that which is in connection with the positive pole of the battery. Mr Brande*, who first observed this phenomenon, ascribes it to the separation of free soda, upon which he supposes the solubility of albumen in water to depend; but M. Lassaigne† attributes it to the decomposition of muriate of soda, the acid of which coagulates the albumen. However this may be, galvanism is one of the most elegant and delicate tests of the presence of albumen in animal fluids which we possess.

Chemists are not agreed as to the cause of the coagulation of albumen. When it is coagulated by different chemical agents, such as tannin and metallic salts, the albumen is thrown down in consequence of forming an insoluble compound with the substance employed; and perhaps this is also the mode by which acids coagulate it. With respect to the agency of heat, alcohol, and probably of acids, a different view must be adopted. The explanation usually given is that proposed by Dr Thomson, who ascribes the solubility of albumen to the presence of free soda, and its coagulation to the removal of the alkali. To this hypothesis, Dr Bostock objects, and with every appearance of justice, that albuminous liquids do not contain a sufficient quantity of free alkali for the purpose. (Medico-Chir. Trans. vol. ii. p. 175.) Were I to hazard an opinion on this subject, it would be the following:—that albumen combines directly with water at the moment of being secreted, at a time when its particles are in a state of minute division; but as its affinity for that liquid is very feeble, the compound is decomposed by slight causes, and for the same reason the albumen becomes quite insoluble, as soon as it is rendered solid by coagulation. Silica affords an instance of a similar phenomenon. (Page 308.)

Albumen coagulates without appearing to undergo any change of composition, but it is quite insoluble in water, and is less liable to putrefy than in its liquid state. It is dissolved by alkalies with disengagement of ammonia, and is precipitated from its solution by acids. In the coagulated state, it bears a very close resemblance to fibrin, and is with difficulty distinguished from it. Alcohol, ether, acids, and alkalies, according to Berzelius, act upon each in the same manner. He observes, however, that acetic acid and ammonia dissolve fibrin more easily than coagulated albumen. According to Thenard, they are readily distinguished by means of the deutoxide of hydrogen, from which fibrin causes evolution of oxygen, while albumen has no action upon it.

Albumen has been analyzed by Gay-Lussac and Thenard, and Dr Prout, with the following results:—

* Philosophical Transactions for 1809.
† An. de Ch. et de Ph. vol. xx.

| | Gay-Lussac and Thenard. | | Dr Prout. | |
|---|---|---|---|---|
| Carbon, | 52.883 | seventeen equiv. | 50. | fifteen equiv. |
| Hydrogen, | 7.540 | thirteen equiv. | 7.78 | fourteen equiv. |
| Oxygen, | 23.872 | six equiv. | 26.67 | six equiv. |
| Nitrogen, | 15.705 | two equiv. | 15.55 | two equiv. |
| | 100.000 | | 100.00 | |

## Gelatin.

Gelatin exists abundantly in many of the solid parts of the body, especially in the skin, cartilages, tendons, membranes, and bones. According to Berzelius, it is not contained in any of the healthy animal fluids; and Dr Bostock, with respect to the blood, has demonstrated the accuracy of this statement. (Medico-Chir. Trans. vol. i. and ii.)

Gelatin is distinguished from all animal principles by its ready solubility in boiling water, and by the solution forming a bulky, semi-transparent, tremulous jelly as it cools. Its tendency to gelatinize is such, that one part of gelatin, dissolved in 100 parts of water, becomes solid in cooling. This jelly is a hydrate of gelatin, and contains so much water, that it readily liquefies when warmed. On expelling the water by a gentle heat, a brittle mass is left, which retains its solubility in hot water, and may be preserved for any length of time without change. Jelly, on the contrary, soon becomes acid by keeping, and then putrefies.

The common gelatin of commerce is the well-known cement called *glue*, which is prepared by boiling in water the cuttings of parchment, or the skins, ears, and hoofs of animals, and evaporating the solution. Isinglass, which is the purest variety of gelatin, is prepared from the sounds of fish of the genus *acipenser*, especially from the sturgeon. The animal jelly of the confectioners is made from the feet of calves, the tendinous and ligamentous parts of which yield a large quantity of gelatin.

Gelatin is insoluble in alcohol, but is dissolved readily by most of the diluted acids, which form an excellent solvent for it. Mixed with twice its weight of concentrated sulphuric acid, it dissolves without being charred; and on diluting the solution with water, boiling for several hours, separating the acid by means of chalk, and evaporating the filtered liquid, a peculiar saccharine principle is deposited in crystals. This substance has a sweet taste, somewhat like that of the sugar of grapes, is soluble in water, though less so than common sugar, and is insoluble in alcohol. When heated to redness, it yields ammonia as one of the products, a circumstance which shows that it contains nitrogen. Mixed with yeast, its solution does not undergo the vinous fermentation; and it combines directly with the nitric acid. It is hence apparent that, though possessed of a sweet taste, it differs entirely from sugar. This substance was discovered by M. Braconnot. (An. de Ch. et de Ph. vol. xiii.)

Gelatin is dissolved by the liquid alkalies, and the solution is not precipitated by acids.

Gelatin manifests little tendency to unite with metallic oxides. Corrosive sublimate and subacetate of lead do not occasion any precipitate in a solution of gelatin, and the salts of tin and silver affect it very slightly. The best precipitant for it is tannin. By means of an infusion of gall-nuts, Dr Bostock detected the presence of gelatin

when mixed with 5000 times its weight of water; and its quantity may even be estimated approximately by this reagent. (Page 476.) But since other animal substances, as for example albumen, are precipitated by tannin, it cannot be relied on as a test of gelatin. The best character for this substance is that of solubility in hot water, and of forming a jelly as it cools.

According to the analysis of gelatin by Gay-Lussac and Thenard, 100 parts of this substance consist of carbon 47.881, hydrogen 7.914, oxygen 27.207, and nitrogen 16.998. From these numbers it appears that its composition, as to the relative quantity of its elements, is identical with that of albumen as determined by Dr Prout.

## *Urea.*

Pure urea is procured by evaporating fresh urine to the consistence of a syrup, and then gradually adding to it, when quite cold, pure concentrated nitric acid, till the whole becomes a dark-coloured crystallized mass, which is to be slightly washed with cold water, and then dried by pressure between folds of bibulous paper. To the nitrate of urea, thus procured, a pretty strong solution of carbonate of potassa or soda is added, until the acid is neutralized; and the solution is afterwards concentrated by evaporation, and set aside, in order that the nitre may separate in crystals. The residual liquid, which is an impure solution of urea, is made up into a thin paste with animal charcoal, and is allowed to remain in that state for a few hours. The paste is then mixed with cold water, which takes up the urea, while the colouring matter is retained by the charcoal; and the colourless solution is evaporated to dryness at a low temperature. The residue is then boiled in pure alcohol, by which the urea is dissolved, and from which it is deposited in crystals on cooling.

Dr Prout, to whom we are indebted for the foregoing process for preparing pure urea, has given the following account of its properties. (Medico-Chir. Trans. vol. viii. p. 529.) Its crystals are transparent and colourless, of a slight pearly lustre, and have commonly the form of a four-sided prism. It leaves a sensation of coldness on the tongue like nitre. Its smell is faint and peculiar, but not urinous. Its specific gravity is about 1.35. It does not affect the colour of litmus or turmeric paper. In a moist atmosphere, it deliquesces slightly; but otherwise undergoes no change on exposure to the air. Exposed to a strong heat, it melts, and is partly decomposed, and partly sublimes, apparently without change. The chief product of the decomposition, besides inflammable gas of a very fetid odour, benzoic acid, and charcoal, is carbonate of ammonia.

Water at 60° dissolves more than its own weight of urea, and boiling water takes up an unlimited quantity. It requires for solution about five times its weight of alcohol of specific gravity 0.816 at 60° F. and rather less than its own weight at a boiling temperature. The aqueous solution of pure urea may be exposed to the atmosphere for several months, or be heated to the boiling point, without change; but, on the contrary, if the other constituents of the urine are present, it putrefies with rapidity, and is decomposed by a temperature of 212° F. being almost entirely resolved into carbonate of ammonia by continued ebullition.

The pure fixed alkalies and alkaline earths decompose urea, especially by the aid of heat, carbonate of ammonia being the chief product.

Though urea has not any distinct alkaline properties, it unites with

the nitric and oxalic acids, forming sparingly soluble compounds, which crystallize in scales of a pearly lustre. This property affords an excellent test of the presence of urea. Both compounds have an acid reaction, and the nitrate consists of 54 parts or one equivalent of nitric acid, and 60 parts or two equivalents of urea.

The constituents of urea, according to the analysis of Dr Prout, are in the proportion of one equivalent of carbon, two of hydrogen, one of oxygen, and one of nitrogen. Its atomic weight, therefore, is 30.

A singular instance of the artificial production of urea has been lately noticed by Wöhler. It is formed by the action of ammonia on cyanogen; but the best mode of preparing it is by decomposing cyanate of silver with muriate of ammonia, or acting on cyanate of lead with ammonia. In the last case, oxide of lead is set free, and the only other product appears in colourless, transparent, four sided, rectangular crystals. These crystals, judging by the mode of preparation, must be cyanate of ammonia. But yet no ammonia is evolved from them by the action of potassa; the stronger acids do not, as with other cyanates, cause an evolution of carbonic and cyanic acids; nor do they yield precipitates with salts of lead and silver. In fact, though procured by the mutual action of cyanic acid and ammonia, the characters above mentioned do not indicate the presence of either; but on the contrary the crystals agree with urea obtained from urine in composition and all their chemical properties. (Journal of Science, N. S. iii. 491.)* The cyanic acid above referred to is that discovered by Wöhler. (Page 254.)

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* This identity of composition between the cyanate of ammonia and urea does not obtain, unless it is assumed that the cyanate contains one equivalent of water. Thus the protohydrated cyanate of ammonia would consist of

| | | | |
|---|---|---|---|
| Cyanic acid, | Carbon, . | 12 | or two equivalents. |
| | Nitrogen, . | 14 | or one equivalent. |
| | Oxygen, . | 8 | or one equivalent. |
| Ammonia, | Nitrogen, . | 14 | or one equivalent. |
| | Hydrogen, . | 3 | or three equivalents. |
| Water, | Oxygen, . | 8 | or one equivalent. |
| | Hydrogen, . | 1 | or one equivalent. |
| | | 60 | |

These proportions are equivalent to

| | | |
|---|---|---|
| Carbon, . | 12 | or two equivalents. |
| Nitrogen, . | 28 | or two equivalents. |
| Oxygen, . | 16 | or two equivalents. |
| Hydrogen, . | 4 | or four equivalents. |
| | 60 | |

Now the composition of urea is,

| | | |
|---|---|---|
| Carbon, . | 6 | or one equivalent. |
| Nitrogen, . | 14 | or one equivalent. |
| Oxygen, . | 8 | or one equivalent. |
| Hydrogen, . | 2 | or two equivalents. |
| | 30 | |

Here it is apparent that the proportions in which the elements are united in the two substances are precisely the same; and that two

## *Sugar of Milk, and Sugar of Diabetes.*

*Sugar of Milk.*—The saccharine principle of milk is obtained from whey by evaporating that liquid to the consistence of syrup, and allowing it to cool. It is afterwards purified by means of albumen and a second crystallization.

The sugar of milk has a sweet taste, though less so than the sugar of the cane, from which it differs essentially in several other respects. Thus it requires seven parts of cold and four of boiling water for solution, and is insoluble in alcohol. It is not susceptible of undergoing the vinous fermentation; and when digested with nitric acid, it yields the saccholactic acid, a property first noticed by Scheele, and which distinguishes the saccharine principle of milk from every other species of sugar. Like starch, it is convertible into real sugar by being boiled in water acidulated with sulphuric acid.

The sugar of milk contains no nitrogen, and, according to the analysis of Gay-Lussac and Thenard, is very analogous to common sugar in the proportion of its elements.

*Sugar of Diabetes.*—In the disease called *diabetes*, the urine contains a peculiar saccharine matter, which, when properly purified, appears identical both in properties and composition with vegetable sugar, approaching nearer to the sugar of grapes than that from the sugar cane.

This kind of sugar is obtained in an irregularly crystalline mass by evaporating diabetic urine to the consistence of syrup, and keeping it in a warm place for several days. It is purified by washing the mass with alcohol either cold or at most gently heated, till that liquid comes off colourless, and then dissolving it in hot alcohol. By repeated crystallization, it is thus rendered quite pure. (Prout.)

Two other principles yet remain to be considered, namely, the colouring principle of the blood, and caseous matter; but these will be more conveniently studied in subsequent sections.

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# SECTION II.

## *ANIMAL ACIDS.*

In animal bodies several acids are found, such as the sulphuric, muriatic, phosphoric, acetic, &c., which belong equally to the mineral or vegetable kingdom, and which have consequently been described in other parts of the work. In this section are included those acids only which are believed to be peculiar to animal bodies.

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equivalents of urea are exactly equal to one equivalent of the hydrated cyanate of ammonia. *North American Med. and Surg. Journal, for Jan.* 1829, *from the Journ. de Chimie Méd.* B.

## *Uric, Purpuric, Rosacic, Formic, and Lactic Acids, &c.*

*Uric or Lithic Acid.*—This acid is a common constituent of urinary and gouty concretions, and is always present in healthy urine, combined with ammonia or some other alkali. The urine of birds of prey, such as the eagle, and of the *boa constrictor* and other serpents, consists almost solely of urate of ammonia, from which pure uric acid may be procured by a very simple process. For this purpose the solid urine of the *boa constrictor* is reduced to a fine powder, and digested in a solution of pure potassa, in which it is readily dissolved with disengagement of ammonia. The urate of potassa is then decomposed by adding the acetic, muriatic, or sulphuric acid in slight excess, when the uric acid is thrown down, and, after being washed, is collected on a filter. On its first separation from the alkali, it is in the form of a gelatinous hydrate, but in a short time this compound is decomposed spontaneously, and the uric acid subsides in small crystals.

Pure uric acid is white, tasteless, and inodorous. It is insoluble in alcohol, and is dissolved very sparingly by cold or hot water, requiring about 10,000 times its weight of that fluid at 60° F. for solution. (Prout.) It reddens litmus paper, and unites with alkalies, forming salts which are called *urates* or *lithates*. The uric acid does not effervesce with alkaline carbonates; but Dr Thomson affirms that when boiled for some time with carbonate of soda, the whole of the carbonic acid is expelled. A current of carbonic acid, on the contrary, throws down the uric acid when dissolved by potassa. This acid undergoes no change by exposure to the air.

Of the acids none exert any peculiar action on the uric excepting the nitric acid. When a few drops of nitric acid, slightly diluted, are mixed on a watch glass with uric acid, and the liquid is evaporated to dryness, a beautiful purple colour comes into view, the tint of which is improved by the addition of water. This character affords an unequivocal test of the presence of uric acid. The nature of the change will be considered immediately.

Uric acid is decomposed by chlorine. On transmitting that gas through water in which uric acid is suspended, the latter disappears, and the liquid is found to contain the oxalic and malic acids, and muriate of ammonia.

Uric acid has been repeatedly analyzed by Dr Prout, and its constituents, according to his latest analysis, (Medico-Chir. Trans. vol. ix.) are in the following proportions:—

| | | | |
|---|---|---|---|
| Carbon, | . | 36 | or six equivalents. |
| Hydrogen, | . | 2 | or two equivalents. |
| Oxygen, | . | 24 | or three equivalents. |
| Nitrogen, | . | 28 | or two equivalents. |
| | | 90 | |

The crystallized acid, as analyzed by Prout, is supposed by most chemists to be anhydrous; but Dr Thomson maintains that on exposing 90 parts of it to a temperature of 400° F. it loses 18 parts, or two equivalents of water, and that the residue is the real anhydrous uric acid, composed of six equivalents of carbon, one of oxygen, and two of nitrogen. On this view, the atomic weight of uric acid is 72, a number which Dr Thomson has deduced from his analysis of the urate of soda.

The salts of uric acid have been described by Dr Henry. (Manchester Memoirs, vol. ii. N.S.) The only ones of importance are the urates of ammonia, potassa, and soda. The urate of ammonia is soluble to a considerable extent in boiling, but more sparingly in cold water. The urates of soda and potassa, if neutral, are of very sparing solubility; but an excess of either alkali takes up a large quantity of the acid. The former was found by Dr Wollaston to be the chief constituent of gouty concretions.

*Pyro-uric Acid.*—When uric acid is exposed to heat in a retort, the carbonate and hydrocyanate of ammonia are formed, together with a peculiar volatile acid, called *pyro-uric acid*, which was formerly described by Dr Henry, and has recently been particularly studied by MM. Chevallier and Lassaigne. (Ann. of Phil. vol. xvi.)

This acid sublimes without change, and condenses on cool surfaces in the form of white acicular crystals. It is soluble in boiling alcohol, and requires forty times its weight of water for solution. It is not decomposed by digestion in nitric acid, a character by which it is distinguished from uric acid.

*Purpuric Acid.*—This compound was first recognised as a distinct acid by Dr Prout, and was described by him in the Philosophical Transactions for 1818. Though colourless itself, it has a remarkable tendency to form red or purple coloured salts with alkaline bases, a character by which it is distinguished from all other substances, and to which it owes the name of *purpuric acid*, suggested by Dr Wollaston. Thus the purple residue above mentioned, as indicative of the presence of uric acid, is the purpurate of ammonia, which is always generated when the uric is decomposed by nitric acid.

This compound is prepared by digesting pure uric acid, extracted from the urine of the *boa constrictor*, in dilute nitric acid, when the former is dissolved with effervescence. The solution is then neutralized by ammonia, and concentrated by evaporation, during the course of which purple coloured crystals of the purpurate of ammonia are deposited. The purpurate of ammonia is then decomposed by digestion with pure potassa, and the liquid is gradually poured into dilute sulphuric acid. The purpuric acid is thus disengaged, and being insoluble in water, subsides to the bottom in the form of a white or yellowish-white powder, according to its degree of purity. This process, I may remark, is one of some delicacy;—I have repeatedly followed the steps recommended by Dr Prout, but have been as frequently disappointed in the attempt to procure the acid in an insulated state.

Considerable uncertainty prevails as to the nature of purpuric acid. Vauquelin, for example, denies that its salts have a purple colour, but attributes that tint to the presence of some impurity. M. Lassaigne is likewise inclined to the same opinion. (An. de Ch. et de Ph. vol. xxij, p. 334.) The composition of the acid is a point equally unsettled; for Dr Prout has expressed a doubt of the accuracy of the analysis which he formerly published.

The name of *erythric acid* (from ἐρυθραίνειν, *to redden*) was applied by Brugnatelli to a substance which he procured by the action of the nitric on uric acid. It obviously contains purpuric acid, and Dr Prout thinks it probable that it is a super-salt, consisting of purpuric and nitric acids, and ammonia.

*Rosacic Acid.*—This name was applied by Proust to a peculiar acid supposed to exist in the red matter, commonly called by medical practitioners the *lateritious sediment*, which is deposited from the some stages of fever. From the experiments of Vogel, it ap- be uric acid, either combined with an alkali, or modified by

the presence of animal matter. Dr Prout is of opinion that it contains some purpurate of ammonia; and, as he has detected the presence of nitric acid in the urine from which such sediments were deposited, he thinks it probable that the purpurate may be generated by he reaction of the uric and nitric acids on each other in the urinary assages.

*Formic Acid.*—The acid extracted from ants was for some time uspected, chiefly on the authority of Fourcroy and Vauquelin, to be mixture of the acetic and malic acids; but the experiments of Suersn, Gehlen, Berzelius, and Döbereiner appear to leave no doubt of s being a distinct compound. In volatility and odour, it does, indeed, semble the acetic acid; but in composition it is entirely different. ccording to the analysis of the formate of lead by Berzelius, the omic weight of formic acid is inferred to be 37; and it is composed carbon 12 parts or two equivalents, hydrogen 1 or one equivalent, id 24 parts or three equivalents of oxygen. It hence differs from xalic acid, only in containing one equivalent of hydrogen. According to Döbereiner, it is resolved into carbonic oxide and water by the tion of strong sulphuric acid. The same ingenious chemist has icceeded in preparing formic acid artificially, by applying a gentle eat to a mixture of tartaric acid, water, and peroxide of manganese. he tartaric acid is converted into water, carbonic acid, and formic cid. (An. of Phil. vol. iv. N. S. 311.)

*Lactic Acid.*—The existence of this acid, though described by Berelius, and found by him in sour milk and in many animal fluids, was ever demonstrated in a satisfactory manner. Berzelius himself now dmits it to be acetic acid disguised by animal matter, an opinion which s confirmed by Tiedemann and Gmelin in their experimental Essay on Digestion. (Die Verdauung nach Versuche. Heidelberg, 1826.)

The *amniotic* is a weak acid which was discovered by Buniva and Vauquelin in the liquor of the amnios of the cow, from which it is leposited by gentle evaporation in the form of white acicular crystals. It is very sparingly soluble in water, but yields with the alkalies soluble compounds which are decomposed by most of the acids.

Several other animal acids, such as the stearic, oleic, margaric, and thers, should also be mentioned here; but as they are closely allied o the fatty principles from which they are derived, they will be more conveniently described in the following section.

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## SECTION III.

### *OLEAGINOUS SUBSTANCES.*

### *Animal Oils and Fats.*

The fatty principles derived from the bodies of animals are very analogous in composition and properties to the vegetable fixed oils; and in Britain, where the latter are comparatively expensive, the former are employed, both for the purposes of giving light, and for the manufacture of soap. Their ultimate elements are carbon, hydrogen, and oxygen; and most of them, like the fixed oils, consist of stearine and elaïne.

From a curious experiment of Bérard, it appears that a substance

very analogous to fat may be made artificially. On mixing together one measure of carbonic acid, ten measures of carburetted hydrogen, and twenty of hydrogen, and transmitting the mixture through a red-hot tube, several white crystals were obtained, which were insoluble in water, soluble in alcohol, and fusible by heat into an oily fluid. (An. of Ph. vol. xii. p. 41.) Döbereiner prepared an analogous substance from a mixture of coal gas and aqueous vapour.

*Train Oil.*—Train oil is obtained by means of heat from the blubber of the whale, and is employed extensively in making oil gas, and for burning in common lamps. It is generally of a reddish or yellow colour, emits a strong unpleasant odour, and has a considerable degree of viscidity, properties which render it unfit for being burned in Argand lamps, and which are owing partly to the heat employed in its extraction, and partly to the presence of impurities. By purification, indeed, it may be rendered more limpid, and its odour less offensive; but it is always inferior to spermaceti oil.

*Spermaceti oil* is obtained from an oily matter lodged in a bony cavity in the head of the *physeter macrocephalus*, or spermaceti whale. On subjecting this substance to pressure in bags, a quantity of pure limpid oil is expressed; and the residue, after being melted, strained, and washed with a weak solution of potassa, is sold under the name of *spermaceti*.

*Animal Oil of Dippel.*—This name is applied to a limpid volatile oil, which is entirely different from the oils above mentioned, and is a product of the destructive distillation of animal matter, especially of albuminous and gelatinous substances. When purified by distillation, it is clear and transparent. It was formerly much used in medicine, but is now no longer employed.

*Hogslard and Suet.*—The most common kinds of fat are hogslard and suet, which differ from each other chiefly in consistence. The latter, when separated by fusion from the membrane in which it occurs, is called tallow, which is extensively employed in the manufacture of soap and candles. Both these varieties of fat, as well as train and spermaceti oil, consist almost entirely of stearine and elaïne; and when converted into soap, undergo the same change as the fixed oils, yielding margaric and oleic acids, and the mild principle of oils called *glycerine*. Stearic acid is also a constituent of soap made from these animal fats.

The method of preparing stearine and elaïne from the vegetable oils has already been detailed, (page 451); and the same process, which originated with M. Braconnot, is also applicable to hogslard. The mode by which M. Chevreul obtains these principles is by treating hogslard in successive portions of hot alcohol. The spirit in cooling deposites the stearine in the form of white crystalline needles, which are brittle, and have the aspect of wax, fuse readily when heated, and are insoluble in water. The alcoholic solution, when evaporated, leaves an oily fluid which is elaïne. They may be then rendered quite pure by re-solution in boiling alcohol.

For a full account of the acids generated, during the formation of soap, by the action of alkaline substances on oil or fat, I refer to the treatise of M. Chevreul, *sur les Corps Gras*. The margaric and oleic acids are best prepared from soap made with potassa and fluid vegetable oil. This soap, after being dried as much as possible, is treated by successive portions of cold alcohol of specific gravity 0.821, in which the oleate of potassa is soluble, and the margarate insoluble. The two salts being thus separated, are decomposed by means of an acid.

Margaric acid, so named from its pearly lustre, (from *μαργαριτης* a

*pearl*) is insoluble in water, and is hence precipitated by acids from the solution of its salts. It is abundantly dissolved by hot alcohol, and is deposited from the saturated solution, in cooling, in a crystalline mass of a pearly lustre. At 140° F. it is fused, and shoots into brilliant white acicular crystals as it cools. It has an acid reaction, and its salts, those of the alkalies excepted, are very sparingly soluble in water. The crystallized acid contains 3.4 per cent of water, and the acid itself consists of 79 parts of carbon, 12 of hydrogen, and 9 of oxygen.

Oleic acid is best prepared from soap made with linseed oil and potassa, since the greater part of it consists of oleate of potassa. This salt is first separated from the margarate of potassa by cold alcohol, and the oleic acid then precipitated from an aqueous solution of the oleate by means of an acid. At the mean temperature, oleic acid is a colourless oily fluid, which congeals when it is cooled to near zero. It has a slightly rancid odour and taste, and reddens litmus paper. Its specific gravity is 0.898. It is insoluble in water, but is dissolved in every proportion by alcohol. Of the neutral oleates hitherto examined, those of soda and potassa are alone soluble in water. In its pure state, it contains 3.8 per cent of water, and consists, the water abstracted, of 80.94 parts of carbon, 11.36 of hydrogen, and 7.7 of oxygen.

*Stearic Acid.*—This acid is best prepared from soap made with potassa and suet or hogslard, and exists in this soap, together with margaric and oleic acids. The soap is dissolved in 6 times its weight of warm water, then mixed with 40 or 50 parts of cold water, and the mixture set aside in a place the temperature of which is about 56°. A precipitate of a pearly lustre gradually collects, consisting of the bimargarate and bistearate of potassa, which are to be collected and well washed upon a filter. The two salts are then separated by repeated solution in about 20 times their weight of boiling alcohol, from which on cooling the whole of the bistearate is deposited, while part of the bimargarate on each occasion is retained in solution. The former is considered pure, when the stearic acid, separated from the potassa by means of another acid, requires a temperature of 158° F. for fusion.

Stearic acid is very similar in its appearance and properties to margaric acid, and the chief ground of distinction between them is in the latter being rather more fusible, and containing rather more oxygen than the former.

*Sebacic Acid.*—M. Thenard has applied this name to an acid, which is obtained by the distillation of hogslard or suet, and is found in the recipient mixed with acetic acid and fat, partially decomposed. It is separated from the latter by means of boiling water, and from the former by the acetate of lead. The sebate of lead, which subsides, is subsequently decomposed by sulphuric acid.

The sebacic acid reddens litmus paper, dissolves freely in alcohol, and is more soluble in hot than in cold water. It melts like fat when heated, and crystallizes in small white needles in cooling. It is not applied to any use.

*Butyrine.*—Butter differs from the common animal fats in containing a peculiar oleaginous matter, which is quite fluid at 70° F. and to which M. Chevreul has applied the name of *butyrine*. When converted into soap, it yields, in addition to the usual products, three volatile odoriferous compounds,-namely, the *butyric*, *caproic* and *capric* acids.

*Phocenine* is a peculiar fatty substance contained in the oil of the

porpoise (*delphinum phocæna*) mixed with elaine. When converted into soap it yields a volatile odoriferous acid, called the *phocenic acid.* (Chevreul.)

*Hircine* is contained in the fat of the goat and sheep, and yields the *hircic acid* when converted into soap. (Chevreul.)

Other acids, more or less analogous to those above described, are formed during the conversion of other oleaginous substances into soap. Thus castor oil yields three acids, to which MM. Bussy and Lecanu have applied the names of *margaritic, ricinic* and *elaiodic* acid. The *cevadic* acid was prepared in a similar manner by Pelletier and Caventou from oil derived from the seeds of the Veratrum sabadilla; and the same chemists have given the name of *jatrophic* acid (more properly *crotonic*) to the acid of the soap made from croton oil. This oil is derived from the seeds of the *Croton tiglium.*

The sweet principle of oils, the *glycerine* of Chevreul, was discovered by Scheele. It was originally obtained in the formation of common plaster by boiling oil with oxide of lead and a little water; and Chevreul found that it is produced during the saponification of fatty substances in general. In preparing soap by means of potassa, the glycerine is left in the mother liquor; and on neutralizing the free alkali with sulphuric acid, evaporating to the consistence of syrup, and treating the residue with alcohol, it is dissolved. The alcoholic solution, when evaporated, yields glycerine in the form of an uncrystallizable syrup. It is soluble in water and alcohol, and has a sweet taste, but is not susceptible either of the vinous or acetous fermentation. According to the analysis of Chevreul, glycerine, of the specific gravity of 1.27, contains 40.071 parts of carbon, 8.925 of hydrogen, and 51.004 of oxygen.

*Spermaceti.*—This inflammable substance, which is prepared from the spermaceti whale as above mentioned, commonly occurs in crystalline plates of a white colour and silvery lustre. It is brittle, and feels soft and slightly unctuous to the touch. It has no taste, and scarcely any odour. It is insoluble in water, but dissolves in about thirteen times its weight of boiling alcohol, from which the greater part is deposited on cooling in the form of brilliant scales. It is still more soluble in ether. It is exceedingly fusible, liquefying at a temperature which is distinctly below 212° F. Digested with pure potassa it is converted into soap, and the acid then generated has received from M. Chevreul the name of *cetic acid.*

The spermaceti of commerce always contains some fluid oil, from which it may be purified by solution in boiling alcohol. To the white crystalline scales deposited from the spirit as it cools, and which is spermaceti in a state of perfect purity, M. Chevreul has given the name of *cetine.*

*Adipocire.*—When a piece of fresh muscle is exposed for some time to the action of water, or is kept in moist earth, the fibrin entirely disappears, and a fatty matter called *adipocire* remains, which has some resemblance to spermaceti. The fibrin was formerly thought to be really converted into adipocire; but Gay-Lussac* and Chevreul maintain that this substance proceeds entirely from the fat originally present in the muscle, and that the fibrin is merely destroyed by putrefaction. Dr Thomson maintains, however, that the conversion of fibrin into fat does not occur in some instances, and has related a remarkable case in proof of his opinion. (Ann. of Phil. vol. xii. p. 41.)

* An. de Ch. et de Ph. vol. iv.

According to M. Chevreul, the adipocire is not a pure fatty principle, but a species of soap, chiefly consisting of margaric acid in combination with ammonia generated during the decomposition of the fibrin.

*Cholesterine**.—This name is applied by M. Chevreul to the crystalline matter which constitutes the basis of most of the biliary concretions formed in the human subject. Fourcroy, regarding it as identical with spermaceti and the fatty matter just described, comprehended all these substances under the general appellation of adipocire; but M. Chevreul has shown that it is a distinct independent principle, wholly different from spermaceti.

Cholesterine is a white brittle solid of a crystalline lamellated structure, and brilliant lustre, very much resembling spermaceti; but it is distinguished from that substance by requiring a temperature of 278° F. for fusion, and by not being convertible into soap when digested in a solution of potassa. It is free from taste and odour, and is insoluble in water. It dissolves freely in boiling alcohol, from which it is deposited on cooling in white pearly scales. According to the analysis of Chevreul, it is composed of 85.095 parts of carbon, 11.88 of hydrogen, and 3.025 of oxygen.

When heated with its own weight of concentrated nitric acid, cholesterine is dissolved with disengagement of nitric oxide gas; and in cooling a yellow matter precipitates, an additional quantity of which may be obtained by dilution with water. This substance possesses the properties of acidity, and is called *cholesteric* acid. It is insoluble in water, but dissolves freely in alcohol, especially with the aid of heat. Its taste is slightly styptic, and its odour somewhat like that of butter; it is lighter than water, and fusible at 136.5° F. In mass it is of an orange-yellow tint; but when the alcoholic solution is evaporated spontaneously, it is deposited in acicular crystals of a white colour. It reddens litmus paper, and neutralizes alkaline bases. The cholesterates of potassa and soda are deliquescent and very soluble in water, but insoluble in alcohol and ether. The cholesterates of the earths and other metallic oxides are either sparingly dissolved by water or altogether insoluble. Its salts are precipitated by the mineral and most of the vegetable acids; but are not decomposed by carbonic acid. For these facts respecting the formation and properties of cholesteric acid, we are indebted to the experiments of MM. Pelletier and Caventou. (Journal de Pharmacie, iii. 292.)

Cholesterine has been detected in the bile of man, and of several of the lower animals, such as the ox, dog, pig, and bear. This interesting discovery was made about the same time by Chevreul in Paris, and by Tiedemann and Gmelin in Heidelburg. M. Lassaigne has likewise found it in the biliary calculus of a pig. (An. de Ch. et de Ph. vol. xxxi.) It is frequently formed in parts of the body quite unconnected with the hepatic circulation, and appears to be a common product of deranged vascular action. M. Caventou, in the Journal de Pharmacie for October 1825, states that the contents of an abscess, formed under the jaw apparently in consequence of a carious tooth, were found by him to consist almost entirely of cholesterine. In the article *calcul* of the *Nouveau Dictionnaire de Medecine*, M. Breschet observes that cholesterine has been found in cancer of the intestines, and in the fluid of hydrocele and ascites in the human subject; and adds that M. Barruel procured it in large quantity from an ovarian cyst in a mare, and in the fluid drawn off from the ovary of a woman, and

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* From χολη *bile*, and στερεος *solid*.

scrotum of a man. M. Breschet has found it also in a tumour under the tongue. Dr Christison found it lately in the fluid of hydrocele, taken from a patient in the Royal Infirmary of Edinburgh by the late Dr William Cullen; in an osseous cyst into which the kidneys of another patient were converted; and in the membranes of the brain of an epileptic patient.

The best method of preparing pure cholesterine is to treat human biliary concretions, reduced to powder, with boiling alcohol, and to filter the hot solution as rapidly as possible. As the liquid cools, the greater part of the cholesterine subsides. In this way it is freed from the colouring matter, with which it is commonly associated in the gall-stone.

*Ambergris.*—This substance is found floating on the surface of the sea near the coasts of India, Africa, and Brazil, and is supposed to be a concretion formed in the stomach of the spermaceti whale. It has commonly been regarded as a resinous principle; but its chief constituent is a substance very analogous to cholesterine, and to which Pelletier and Caventou have given the name of *ambreine*. By digestion in nitric acid, ambreine is converted into a peculiar acid called the *ambreic acid*. (An. of Phil. vol. xvi.)

# ON THE MORE COMPLEX ANIMAL SUBSTANCES, AND SOME FUNCTIONS OF ANIMAL BODIES.

## SECTION I.

### *ON THE BLOOD, RESPIRATION, AND ANIMAL HEAT.*

The blood, while circulating in the vessels of living animals, is fluid, and of a florid red colour in the arteries, and of a dark purple colour in the veins. Its taste is slightly saline, its odour peculiar, and to the touch it seems somewhat unctuous. Its specific gravity is variable, but most commonly is near 1.05, and in man its temperature is about 98° or 100° Fahr. When recently drawn, it appears to the naked eye as a uniform homogeneous fluid; but if examined with a microscope of sufficient power, numerous red particles of a globular form are seen floating in a colourless fluid. The compound nature of the blood is rendered still more apparent by the process of coagulation, during which it separates spontaneously into two distinct portions, a yellowish liquid called the *serum* of the blood, and a red solid, known by the name of the *clot*, *cruor*, or *crassamentum*. The proportion of these parts is variable, the latter being more abundant in healthy vigorous animals, than in those which have been debilitated by depletion, low living, or disease.

The serum is somewhat unctuous to the touch, of a saline taste, and of slightly alkaline reaction, owing to the presence of a little free so-

da. Its average specific gravity is about 1.029. Like other albuminous liquids, it is coagulated by heat, acids, alcohol, and all other substances which coagulate albumen. On subjecting the coagulum prepared by heat to gentle pressure, a small quantity of a colourless limpid fluid, called the *serosity*, oozes out, which contains according to Dr Bostock about 1-50th of its weight of animal matter, together with a little muriate of soda. Of this animal matter a portion is albumen, which may easily be coagulated by means of galvanism; but a small quantity of some other principle is present, which differs both from albumen and gelatin. (Medico-Chir. Trans. vol. ii. p. 166.)

From the analysis of the late Dr Marcet, 1000 parts of the serum of human blood are composed of water 900 parts, albumen 86.8, muriates of potassa and soda 6.6, muco-extractive matter 4, carbonate of soda 1.65, sulphate of potassa 0.35, and of earthy phosphates 0.60. This result agrees very nearly with that obtained by Berzelius, who states that the *extractive matter* of Marcet is lactate (acetate) of soda united with animal matter. (Medico-Chir. Trans. vol. iii. p. 231.)

The crassamentum or clot of the blood consists of two parts, the fibrin and colouring principle. The latter resides in distinct particles, which, according to Prevost and Dumas, are elliptical in birds and cold-blooded animals, and assume the globular form in the mammiferous animals. These globules are insoluble in serum; but their colour is dissolved by pure water, acids, alkalies, and alcohol. Much uncertainty prevails among chemists relative to the cause of the colour of the red globules. As soon as the blood was known to contain iron, the peroxide of which has a red tint, the colour of the red globules was ascribed to the presence of that metal, and some chemists supposed it to be in the form of the subphosphate of iron. This opinion was adopted by Fourcroy and Vauquelin, who even affirmed that the phosphate of iron may be dissolved in serum by means of an alkali, and that the colour of the solution is exactly similar to that of the blood.

This subject was investigated in the year 1806 by Berzelius, who showed that the subphosphate of iron cannot be dissolved in serum, in the way supposed by Fourcroy and Vauquelin, except in very minute quantity; and that this salt, even when rendered soluble by phosphoric acid, communicates a tint quite different from that of the red globules. On comparing together the composition of the three principal ingredients of the blood, viz. fibrin, albumen, and colouring matter, he found that the ashes of the last always yielded oxide of iron in the proportion of 1-200th of the original mass, while the oxide was entirely wanting in the two former. From this it was a probable inference, that iron is somehow or other concerned in the production of the red colour; but the experiments of Berzelius did not make known the state in which that metal exists in the blood. He could not detect its presence by any of the liquid tests. (Medico-Chir. Trans. vol. iii. p. 213.)

In a series of experiments published in 1812, (Philos. Trans.) Mr Brande obtained results quite contrary to those of Berzelius. He detected iron in the ashes of the serum and fibrin as well as those of the red globules; and in each it was present in such minute quantity, that no effect as a colouring agent could be expected from it. Mr Brande supposed that the tint of the red globules is produced by a peculiar animal colouring principle, capable, like other substances of a similar nature, of combining with metallic oxides. He succeeded in obtaining a compound of the colouring matter of the blood with the oxide of tin; but its best precipitants are nitrate of mercury and corrosi-

sublimate. Woollen cloths impregnated with either of these compounds, on being dipped into an aqueous solution of the colouring matter, acquired a permanent red dye, unchangeable by washing with soap.

The conclusions of Brande, relative to the presence of iron in the albumen and fibrin of the blood received additional support from the researches of Vauquelin; (An. de Ch. et de Ph. vol. i.) but the question has been finally decided by Dr Engelhart, a young German chemist of great promise, who gained the prize offered in the year 1825 by the Medical Faculty of Göttingen for the best essay on the nature of the colouring matter of the blood. (Edinb. Med. and Surg. Journal for January 1827.) He demonstrated that the fibrin and albumen of the blood, when carefully separated from colouring particles, do not contain a trace of iron; and on the contrary, he procured iron from the red globules by incineration. But he has likewise succeeded in proving the existence of iron in the colouring matter of the blood by the liquid tests; for, on transmitting a current of chlorine gas through a solution of the red globules, the colour entirely disappeared, white flocks were thrown down, and a transparent solution remained, in which the peroxide of iron was discovered by all the usual reagents. The results obtained by Dr Engelhart relative to the quantity of the iron, correspond with those of Berzelius. These facts have been since confirmed by M. Rose, who has accounted in a satisfactory manner for the failure of former chemists in detecting iron in the blood while in a fluid state. He finds that the oxide of iron cannot be precipitated by the alkalies, hydrosulphuret of ammonia, or infusion of galls, if it is dissolved in a solution which contains albumen or other soluble organic principles.

From the presence of iron in the red globules, and its total absence in the other principles of the blood, it is probable that this metal, though its quantity does not exceed one-half per cent, is essential to the production of the red colour. The experiments of Dr Engelhart, however, have not determined the manner in which it acts, nor in what state it exists in the blood, though it is most probably in the form of an oxide. It is a singular coincidence that the sulphocyanic acid, which forms with the peroxide of iron a colour exactly like that of venous blood, has been detected in the saliva. The existence of this acid in the blood itself is, therefore, a circumstance by no means improbable.

Dr Engelhart is likewise the first chemist who has procured the colouring matter of the blood in a state of perfect purity. The method formerly recommended is that of Berzelius, whose process consists in allowing the clot, cut into thin slices, to drain as much as possible on bibulous paper, triturating it with water, and then evaporating the solution at a temperature not exceeding 122° F. As thus prepared, the colouring matter retains all its properties, but is mixed with a little serum. The method of Dr Engelhart is founded on the fact, that serum, when much diluted, does not coagulate by heat, while the red particles are coagulated, and fall down in the form of brown flocks. Serum diluted with ten parts of water, does not coagulate at 160° F.; but the colouring matter, dissolved in fifty parts of water, begins to coagulate at 149° F.

The colouring particles, when prepared in this way, are no longer of a bright red colour, and their nature is somewhat modified, in consequence of which they are insoluble in water. When half dried, they form a brownish-red, granular, friable mass; and when completely dried at a temperature between 167° and 190°, the mass is tough, hard, brilliant, black with reflected, and garnet-red with transmitted light.

Except in their insolubility, they have all the properties of the red particles obtained by the method of Berzelius. The caustic alkalies with the aid of heat dissolve them entirely, and the solution acquires a dark blood-red colour.

The fibrin of the blood may easily be obtained in a pure state by washing the clot in cold water until the colouring matter is entirely removed. While circulating in the animal body, it is either in a fluid state, or suspended in the serum in the form of minute colourless globules; but when removed from the vessels and set at rest, it becomes solid in the course of a few minutes, giving rise to what is called the *coagulation* of the blood. The time required for coagulation is influenced by temperature, being promoted by heat, and retarded by cold. Dr Scudamore finds that blood which begins to coagulate in four minutes and a half in an atmosphere of 53° F. undergoes the same change in two minutes and a half at 98°; and that which coagulates in four minutes at 98° will become solid in one minute at 120°. On the contrary, blood which coagulates firmly in five minutes at 60° will remain quite fluid for twenty minutes at the temperature of 40°, and requires upwards of an hour for complete coagulation. (Scudamore on the Blood.)

The process of coagulation is influenced by exposure to the air. If atmospheric air be excluded, as by filling a bottle completely with recently drawn blood, and closing the orifice with a good stopper, coagulation is retarded. It is singular, however, that if blood be confined within the exhausted receiver of an air-pump, the coagulation is accelerated. (Scudamore.)

Recently drawn blood, owing doubtless to its temperature, is known to give off a portion of aqueous vapour, which has a peculiar odour, indicative of the presence of some peculiar principle, but in which nothing but water can be detected. Physiologists are not agreed upon the question whether the act of coagulation is or is not accompanied with the disengagement of gaseous matter. In the experiments of Vogel, Brande, and Scudamore, blood coagulating in the vacuum of an air-pump was found to emit carbonic acid, and Dr Scudamore even inferred that the evolution of this gas constitutes an essential part of the process. Other experimentalists, however, have obtained a different result. Dr John Davy and Dr Duncan, jun. failed in their attempts to procure carbonic acid from blood during coagulation; and Dr Christison, in an experiment performed two years ago in my laboratory, and at which I was present, was not more successful. These facts appear conclusive against the opinion of Dr Scudamore, and they receive additional weight from the consideration, that the appearance of carbonic acid in the experiments above mentioned, might easily have been occasioned by casual exposure to the atmosphere previous to the blood being placed under the receiver.

Coagulation is influenced by the rapidity with which the blood is removed from the body. Dr Scudamore observed, that blood slowly drawn from a vein coagulates more rapidly than when taken in a full stream.

Experiments are still wanting to show the influence of different gases on coagulation. Oxygen gas accelerates coagulation, and carbonic acid retards, but cannot prevent it.

Caloric is evolved during the coagulation of the blood. The late Dr Gordon estimated the rise of the thermometer at six degrees; and Dr Davy, on the other hand, regards the increase of temperature from this cause as very slight. Dr Scudamore finds that the rate at which blood cools is distinctly slower than it would be were no caloric dis-

engaged, and he observed the thermometer to rise one degree at the commencement of coagulation.

Some substances prevent the coagulation of the blood. This effect is produced by a saturated solution of muriate of soda, muriate of ammonia, or nitre, and a solution of potassa. The coagulation, on the contrary, is promoted by alum, and the sulphates of zinc and copper. The blood of persons who have died a sudden violent death, by some kinds of poison, or from mental emotion, is usually found in a fluid state. Lightning is said to have a similar effect; but Dr Scudamore declares this to be an error. Blood, through which electric discharges were transmitted, coagulated as quickly as that which was not electrified; and in animals killed by the discharge of a powerful galvanic battery, the blood in the veins was always found in a solid state.

The cause of the coagulation of the blood has been the subject of much speculation to physiologists. The tendency of this fluid to preserve the liquid form while contained in a living animal, cannot be ascribed to the motion to which it is continually subject within the vessels. It is a familiar fact, that blood, though continually stirred out of the body, is not prevented from coagulating; and it has been noticed, that the coagulation of blood, which is set at rest within its proper vessels by the application of ligatures, or which has been accidentally extravasated within the body, is materially retarded. It has, indeed, been hitherto found impossible to account in a satisfactory manner for the blood retaining its fluidity from the influence of motion, temperature, or the operation of any physical or chemical laws; and, consequently, it is generally ascribed to the agency of the vital principle. The blood is supposed either to be endowed with a principle of vitality, or to receive from the living parts with which it is in contact a certain vital impression, which, together with constant motion, counteracts its tendency to coagulate.

The clot of blood drawn from an individual in a state of health is red throughout its whole substance, because the fibrin coagulates before the red globules have had time to subside. In inflammatory diseases, on the contrary, the blood undergoes a peculiar change, in consequence of which the red globules sink to the bottom before the fibrin has become solid, and thus leave the upper surface of the latter of its natural pale colour. This appearance is familiarly known by the name of *buffy coat.* Its formation must obviously depend either on the coagulation being unusually slow, so that the red globules have full leisure to subside; or on the coagulation taking place in the ordinary period, while the red globules subside with unusual rapidity. The nature of the change which gives rise to the buffy coat is altogether unknown.

## *Respiration.*

When venous blood is brought into contact with atmospheric air, its surface passes from a dark purple to a florid red colour, oxygen disappears, and carbonic acid gas is emitted. These changes take place more speedily when air is agitated with blood; they are still more rapid when pure oxygen is substituted for atmospheric air; and they do not occur at all when oxygen is entirely excluded. It is hence inferred that the process of *arterialization,* as it is called, or the conversion of venous into arterial blood, depends entirely on the presence of oxygen. It is also presumed that the alternating shades of colour are caused by the red particles undergoing certain chemical changes, the nature of which, however, is at present quite inexplicable.

The same changes that occur out of the body are continually taking place within it. During respiration, venous blood is exposed in the lungs to the agency of the air, and is arterialized, oxygen gas disappears, and carbonic acid is evolved; and it is remarkable that these phenomena ensue not only during life, but even after death, provided the respiratory process be preserved artificially. Since, therefore, the essential phenomena of arterialization, according to the best data we possess, are the same in a living and in a dead animal, and whether the blood is or is not contained in the body, it seems quite legitimate to infer, that this process is not necessarily dependent on the vital principle, but is solely determined by the laws of chemical action.

In studying the subject of respiration, the first object is to determine the precise change produced in the constitution of the air which is inhaled. Dr Black was the first to notice that the air exhaled from the lungs contains a considerable quantity of carbonic acid, which may be detected by transmission through lime-water. Priestley, some years after, observed that air is rendered unfit for supporting flame or animal life by the process of respiration, from which it was probable that oxygen is consumed; and Lavoisier subsequently established the fact, that during respiration oxygen gas disappears, and carbonic acid is disengaged. The chief experimentalists who have since cultivated this department of chemical physiology are Priestley, Scheele, Lavoisier, Seguin, Crawford, Goodwin, Davy, Ellis, Allen and Pepys, Edwards and Despretz. Of these, the results obtained by Messrs Allen and Pepys,* and Dr Edwards,† are the most conclusive and satisfactory, their researches having been conducted with great care, and aided by all the resources of modern chemistry.

One of the chief objects of Messrs Allen and Pepys, in their experiments, was to ascertain if any uniform relation exists between the oxygen consumed and the carbonic acid evolved. They found in general that the quantity of the former exceeds that of the latter; but as the difference was very trifling, they inferred that the carbonic acid of the expired air is exactly equal to the oxygen which disappears. The experiments of Dr Edwards were attended with a remarkable result, which accounts very happily for some of the discordant statements of preceding inquirers. He found the ratio between the gases to vary with the animal. In some animals it might be regarded as nearly equal; while in others the loss of oxygen considerably exceeded the gain of carbonic acid, so that the respired air suffered a material diminution in volume. With respect to the human subject, the statement of Allen and Pepys seems very near the truth.

The quantity of oxygen withdrawn from the atmosphere, and of carbonic acid disengaged, is variable in different individuals, and in the same individual at different times. It is estimated by Allen and Pepys, that in every minute during the calm respiration of a healthy man of ordinary stature, 26.6 cubic inches of carbonic acid of the temperature of 50° F. are emitted, and an equal volume of oxygen withdrawn from the atmosphere. From these data it has been calculated, that in an interval of twenty-four hours not less than eleven ounces of carbon are given off from the lungs alone,—an estimate which must surely be inaccurate, the quantity being so great as sometimes to exceed the weight of carbon contained in the food. From the observations of Dr Prout, it appears that the quantity of carbonic

* Philosophical Transactions for 1808.

† De l'Influence des Agens Physiques sur la vie, 1824.

acid emitted from the lungs is variable at particular periods of the day, and in particular states of the system. It is more abundant during the day than the night; about day-break it begins to increase, continues to do so till about noon, and then decreases until sunset. During the night it seems to remain uniformly at a minimum; and the maximum quantity given off at noon, exceeds the minimum by about one-fifth of the whole. The quantity of carbonic acid is diminished by any debilitating causes, such as low diet, depressing passions, and the like. (Ann. of Phil. vol. xiii. p. 269.) The experiments of Dr Fyfe, published in his Inaugural Dissertation, are confirmatory of those above mentioned.

Messrs Allen and Pepys have shown that the atmospheric air, when drawn into the lungs, returns charged in the succeeding expiration with from 8 to 8.6 per cent of carbonic acid gas. They found also, that when an animal is confined in the same quantity of air, death ensues before all the oxygen is consumed; that when the same portion of air is repeatedly respired until it can no longer support life, it then contains only 10 per cent of carbonic acid.

Although in respiration the arterialization of the blood by means of free oxygen is the essential change, without the due performance of which the life of warm-blooded animals cannot be preserved beyond a few minutes, and which is likewise necessary to the lowest of the insect tribe, it is important to determine whether the nitrogen of the atmosphere has any influence in the function. The results of different inquirers differ considerably. In the experiments of Priestley, Davy, Humboldt, Henderson, and Pfaff, there appeared to be absorption of nitrogen, a less quantity of that gas being exhaled than was inspired. Nysten, Berthollet, and Despretz, on the contrary, remarked an increase in the bulk of the nitrogen; and from the researches of Seguin and Lavoisier, Vauquelin, Ellis, Dalton, and Spallanzani, it was inferred that there is neither absorption nor exhalation of nitrogen, the quantity of that gas undergoing no change during its passage through the air cells of the lungs. Messrs Allen and Pepys arrived at a similar conclusion; and since the appearance of their essay, the opinion has prevailed very generally among physiologists, that in respiration the nitrogen of the air is altogether passive.

The facts ascertained by Dr Edwards relative to this subject are novel and of peculiar interest. This acute physiologist has reconciled the discordant results of preceding experimenters, by showing that, during the respiration even of the same animal, the quantity of nitrogen may one while be increased, at another time diminished, and at a third wholly unchanged. He has traced these phenomena to the influence of the seasons; and he suspects, as indeed is most probable, that other causes, independently of season, have a share in their production. In nearly all the lower animals which were made the subjects of experiment, an augmentation of nitrogen was observable during summer. Sometimes, indeed, it was so slight that it might be disregarded. But in many other instances, it was so great as to place the fact beyond the possibility of doubt; and on some occasions, it almost equalled the whole bulk of the animal. Such continued to be the result of his inquiries until the close of October, when he observed a sensible diminution of nitrogen, and the same continued throughout the whole of winter and the beginning of spring.

There are two modes of accounting for these phenomena. According to one view, the nitrogen which disappears is ascribed to the absorption of what was inhaled, and its increase to direct exhalation, the opposite processes of absorption and exhalation being supposed

not to occur at the same moment. According to the other view, both these processes are always going on at the same time, and the result depends on the preponderance of one over the other. When the absorption prevails, a smaller quantity of nitrogen is exhaled than was inspired; when the exhalation exceeds the absorption, an increase of nitrogen takes place; but when the absorption and exhalation are equal, the bulk of the inspired air, so far as nitrogen is concerned, does not undergo any change. The latter opinion, which is adopted by Dr Edwards, is supported by two decisive experiments performed by Messrs Allen and Pepys, in one of which a guinea-pig was confined in a vessel of oxygen gas, and in the other in an atmosphere composed of 21 measures of oxygen and 79 of hydrogen. In both cases the residual air contained a quantity of nitrogen greater than the bulk of the animal itself; and in the last a portion of hydrogen had disappeared. From this it follows that nitrogen may be exhaled from the lungs, and that hydrogen may be absorbed.

Two theories have been proposed in order to account for the phenomena of respiration. According to one theory, the carbonic acid found in the respired air is actually generated in the lungs themselves; while, according to the other, this gas is thought to exist ready formed in the blood, and to be merely thrown off from that liquid during its distribution through the lungs.

The former theory, which appears to have originated with Priestley, has received several modifications. Priestley imagined that the phenomena of respiration are owing to the disengagement of phlogiston from the blood, and its combination with the air. Dr Crawford modified this doctrine in the following manner. (Crawford on Animal Heat.) He was of opinion that venous blood contains a peculiar compound of carbon and hydrogen, termed *hydrocarbon*, the elements of which unite in the lungs with the oxygen of the air, forming water with the one, and carbonic acid with the other; and that the blood, thus purified, regains its florid hue, and becomes fit for the purposes of the animal economy.

The hypothesis of Crawford, however, is not merely liable to the objection that the supposed hydrocarbon, as respects the blood, is quite imaginary, but was found at variance with the leading facts established by Messrs Allen and Pepys. By the elaborate researches of these chemists, it was established that carbonic acid gas contains its own volume of oxygen; and they also concluded that air, inhaled into the lungs, returns charged with a quantity of carbonic acid, almost exactly equal in bulk to the oxygen which disappears, an inference which, as applied to man and some of the lower animals, seems very near the truth. A review of these circumstances induced them to adopt the opinion, that the oxygen of the air combines in the lungs exclusively with carbon; and that the watery vapour, which is always contained in the breath, is an exhalation from minute pulmonary vessels. They conceived that the fine animal membrane interposed between the blood and the air does not prevent chemical action from taking place between them.

This view has been further modified by Mr Ellis, who supposes that the carbon is separated from the venous blood by a process of secretion, and that then, coming into direct contact with oxygen, it is converted into carbonic acid. (Inquiry, &c. Parts I. and II.)

The circumstance which led Mr Ellis to this opinion, was a disbelief in the possibility of oxygen acting upon the blood through the animal membrane in which it is confined. The experiments adduced in proof of the impermeability of membranous substances are not,

however, quite satisfactory; while, on the contrary, the facts noticed by several accurate observers, appear to leave no doubt that moist animal membranes, even in the living body, are in some way or other permeable to substances in a gaseous form.*

According to the second theory, which was supported by La Grange and Hassenfratz, and has lately been adopted by Dr Edwards, carbonic acid generated during the course of the circulation, is given off from the venous blood in the lungs, and oxygen gas is absorbed. This doctrine, though generally regarded hitherto as less probable than the preceding, is supported by very powerful arguments. The experiments and observations of Dr Edwards seem to leave no doubt that the blood, while circulating through the lungs, is capable of absorbing hydrogen, nitrogen, and oxygen gases, and of emitting nitrogen; and he has gone very far towards proving that the carbonic acid is derived from the same source. On confining frogs and snails for some time in an atmosphere of hydrogen, the residual air was found to contain a quantity of carbonic acid, which was in some instances even greater than the bulk of the animal; and a similar result was obtained with young kittens.

The confined limits of the present work do not admit of an examination into the respective advantages and disadvantages of these two theories. I shall merely observe, therefore, that, in the present stage of the inquiry, the deficiency of precise data prevents the establishment of one of them in preference to the other; but that the arguments preponderate in favour of the last.

The conversion of venous into arterial blood appears not to be confined to the lungs. The disengagement of carbonic acid from the surface of the skin, and the corresponding disappearance of oxygen gas was demonstrated by the experiments of Jurine and Abernethy; and although the accuracy of their results has been doubted by some persons, it has been confirmed by others. However this may be in the human subject, the fact with respect to many of the lower animals is unquestionable. Spallanzani proved that some animals possessed of lungs, such as serpents, lizards, and frogs, produce the same changes on the air by means of their skin, as by their proper respiratory organs; and Dr Edwards, in a series of masterly experiments, has shown that this function compensates so fully for the want of respiration by the lungs, as to enable these animals, in the winter season, to live for an almost unlimited period under the surface of water.

## *Animal Heat.*

The striking analogy between the processes of combustion and respiration, in both of which oxygen gas disappears, and an oxidized body is substituted for it, led Dr Black to infer that the caloric generated in the animal system, by means of which the more perfect animals preserve their temperature above that of the surrounding medium, is derived from the changes going forward in the lungs. But this opinion is not founded on analogy alone; many circumstances conspire to show that the development of animal heat is dependent on the function of respiration, although the mode by which the effect is produced has not hitherto been satisfactorily determined. Thus, in

* See some judicious remarks on this subject in the Essay on Respiration and Animal Heat, by Dr Williams, in the Medico-Chir. Trans. of Edinburgh, vol. ii.

all animals, whose respiratory organs are small and imperfect, and which, therefore, consume but a comparatively minute quantity of oxygen, and generate little carbonic acid, the temperature of the blood varies with that of the medium in which they live. In warm-blooded animals, on the contrary, in which the respiratory apparatus is larger, and the chemical changes more complicated, the temperature is almost uniform; and those have the highest temperature whose lungs, in proportion to the size of their bodies, are largest, and which consume the greatest quantity of oxygen. The temperature of the same animal at different times is connected with the state of the respiration. When the blood circulates sluggishly, and the temperature is low, the quantity of oxygen consumed is comparatively small; but, on the contrary, a large quantity of that gas disappears when the circulation is brisk, and the power of generating heat energetic. It has also been observed, especially by Crawford and De Laroche, that when an animal is placed in a very warm atmosphere, so as to require little heat to be generated within his own body, the consumption of oxygen is unusually small, and the blood within the veins retains the arterial character.

The connection between the power of generating heat, and respiration has been illustrated in a very pointed manner by Dr Edwards. Some young animals, such as puppies and kittens, require so small a quantity of oxygen for supporting life, that they may be deprived of that gas altogether for twenty minutes without material injury; and it is remarkable that so long as they possess this property, the temperature of their bodies sinks rapidly by free exposure to the air. But as they grow older they become able to maintain their own temperature, and at the same time their power to endure the privation of oxygen ceases. The same observation applies to young sparrows, and other birds which are naked when hatched; while young partridges, which are both fledged and able to retain their own temperature at the period of quitting the shell, die when deprived of oxygen as rapidly as an adult bird.

The first consistent theory of the production of animal heat was proposed by Dr Crawford. This theory was founded on the assumption that the carbonic acid contained in the breath is generated in the lungs, and that its formation is accompanied with the disengagement of caloric. But since the temperature of the lungs is not higher than that of other internal organs, and arterial very little if at all warmer then venous blood, it follows that the greater part of the caloric, instead of becoming free, must in some way or other be rendered insensible. Accordingly, on comparing the specific caloric of arterial and venous blood, Dr Crawford found the capacity of the former to exceed that of the latter in the ratio of 1030 to 892. He, therefore, inferred that the dark blood within the veins, at the moment of being arterialized, acquires an increase of insensible caloric; and that while circulating through the body, and gradually resuming the venous character, it suffers a diminution of capacity, and evolves a proportional degree of heat.

Unfortunately for the hypothesis of Crawford, one of the leading facts on which it is founded has been called in question; Dr Davy maintaining, on the authority of his own experiments, that there is little or no difference between the capacities of venous and arterial blood. (Philos. Trans. for 1814.) If this be true, the hypothesis itself necessarily falls to the ground. One part of the doctrine of Crawford may, however, in a modified form, be applied to the theory of respiration advocated by Dr Edwards. For if oxygen be absorbed by

the blood in its passage through the lungs, and carbonic acid, ready formed, be emitted in return, it follows that this gas must be generated during the course of the circulation; and it may be inferred, that the heat developed in consequence of this chemical change, is at once communicated to the adjacent organs. In this way the question concerning the capacity of the blood for caloric may be entirely disregarded.

While some physiologists have been disposed to refer the source of animal heat entirely to the alternate changes of venous to arterial, and of arterial to venous blood; others have denied its agency altogether, ascribing the evolution of caloric solely to the influence of the nervous system. The chief foundation for this opinion is in the experiments of Mr Brodie, who inflated the lungs of animals recently killed by narcotic poisons or divisions of the spinal marrow. (Phil. Trans. for 1811 and 1812.) In an animal so treated, the blood continued to circulate, the phenomena of arterialization took place with regularity, oxygen gas disappeared, and carbonic acid was evolved; but notwithstanding the concurrence of all these circumstances, the temperature fell with equal if not greater rapidity than in another animal killed at the same time, but in which artificial respiration was not performed.

Were these experiments rigidly exact, they would lead to the opinion that no caloric is evolved by the mere process of arterialization. This inference, however, cannot be admitted for two reasons:—first, because other physiologists, in repeating the experiments of Brodie, have found that the process of cooling is retarded by artificial respiration; and, secondly, because it is difficult to conceive why the formation of carbonic acid, which uniformly gives rise to increase of temperature in other cases, should not be attended, within the animal body, with a similar effect. It may hence be inferred, that this is one of the sources of animal heat. It is certain, however, that the heat of animals cannot be maintained by the sole process of arterialization. Consistently with this fact, the researches of Dulong and Despretz agree in proving in opposition to the results obtained by Lavoisier and Crawford, that a healthy animal imparts to surrounding bodies a quantity of heat considerably greater than can be accounted for by the combustion of the carbon thrown off during the same interval from the lungs, in the form of carbonic acid. (Ann. de Ch. et Ph. xxvi.)

Though the influence of the nervous system over the development of animal heat is no longer doubtful, physiologists are not agreed as to the mode by which it operates. Its action may either be direct or indirect; that is, the nerves may possess some specific power of generating heat, or they may excite certain operations by which the same effect is occasioned. It is far from improbable, that the nerves act more by the latter than the former mode; that the infinite number of chemical phenomena going on in the minute arterial branches during the processes of secretion and nutrition, processes which are entirely dependent on the nervous system, are attended with disengagement of caloric. This view has, at least, been ably defended by Dr Williams in the essay to which I have already referred.

## SECTION II.

### *ON THE SECRETED FLUIDS SUBSERVIENT TO DIGESTION.*

### *Saliva. Pancreatic and Gastric Juices.*

*Saliva.*—The saliva is a slightly viscid liquor, secreted by the salivary glands. When mixed with distilled water, a flaky matter subsides, which is mucus, derived apparently from the lining membrane of the mouth. The clear solution, when exposed to the agency of galvanism, yields a coagulum, and is hence inferred by Mr Brande to contain albumen; but the quantity of this principle is so very small that its presence cannot be demonstrated by any other reagent. The greater part of the animal matter remaining in the liquid is peculiar to the saliva, and may be termed *salivary matter.* It is soluble in water, insoluble in alcohol, and, when freed from the accompanying salts, is not precipitated by subacetate of lead, corrosive sublimate, or infusion of nut-galls. The saliva likewise contains a small quantity of animal matter, which is soluble both in alcohol and water, and which is supposed by Tiedemann and Gmelin to be osmazome.

The solid contents of the saliva, according to Berzelius, do not exceed 7 in 1000 parts, the rest being water. From the recent analysis of Tiedemann and Gmelin, the chief saline constituent is muriate of potassa; but several other salts, such as the sulphate, phosphate, acetate, carbonate, and sulphocyanate of potassa, are likewise present in small quantity. The saliva of the human subject, according to the same authority, contains very little soda. The property which the saliva possesses of striking a red colour with a per-salt of iron is owing to the sulphocyanate of potassa. This salt exists also in the saliva of the sheep; but it has not been found in that of the dog. The saliva of the sheep contains so much carbonate of soda, that it effervesces with acids.

The only known use of the saliva is to form a soft pulpy mass with the food during mastication, so as to reduce it into a state fit for being swallowed with facility, and for being more readily acted on by the juices of the stomach.

Concretions are sometimes found in the salivary glands and ducts. A stone contained in the salivary gland of an ass was found by M. Caventou to contain 91.6 parts of carbonate of lime, 4.8 of phosphate of lime, and 3.6 of animal matter. A salivary concretion of a horse was found by M. Henry, jun. to consist of carbonate of lime 85.52, carbonate of magnesia 7.56, phosphate of lime 4.40, and 2.48 of animal matter. Carbonate of lime is the chief ingredient of salivary concretions.

*Pancreatic Juice.*—This fluid is commonly supposed to be analogous to the saliva, but it appears from the analysis of Tiedemann and Gmelin that it is essentially different. The chief animal matters are albumen, and a substance like curd; but it also contains a small quantity of salivary matter and osmazome. It reddens litmus paper, owing to the presence of free acid, which is supposed to be the acetic. Its salts are nearly the same as those contained in the saliva,

except that the sulphocyanic acid is wanting. The uses of this fluid are entirely unknown.

*Gastric Juice.*—The gastric juice collected from the stomach of an animal killed while fasting, is a transparent fluid which has a saline taste, and has neither an acid nor alkaline reaction. During the process of digestion, on the contrary, it is found to be distinctly acid. Thus free muriatic acid was detected under these circumstances by Dr Prout* in the stomach of the rabbit, hare, horse, calf, and dog; and he has discovered the same acid in the sour matter ejected from the stomach of persons labouring under indigestion, a fact which has since been confirmed by Mr Children. Messrs Tiedemann and Gmelin have observed that the secretion of acid commences as soon as the stomach receives the stimulus of food or any foreign body. This effect is occasioned, for example, by the presence of flint stones or other indigestible matters; but it is produced in a still greater degree by substances of a stimulating nature. According to their observation, the acidity is owing to the secretion of free muriatic and acetic acids.

The gastric juice coagulates milk, and it is generally supposed to produce this effect quite independently of the presence of an acid. According to the experiments of Spallanzani and Stevens, it is highly antiseptic, not only preventing putrefaction, but rendering meat fresh after it is tainted. But of all the properties of the gastric juice, its solvent virtue is the most remarkable, being that on which depends the first stage of the process of digestion. When the food is introduced into the stomach, it is there intimately mixed with the gastric juice, by the agency of which it is dissolved, and converted into a semi-fluid matter called *chyme*. That this change is really owing to the solvent power of the gastric juice fully appears from the researches of Spallanzani, Reaumur, and Stevens. In the experiments of Dr Stevens, described in his Inaugural Dissertation, the common articles of food were enclosed in hollow silver spheres perforated with holes, and after remaining for some time within the stomach, completely protected from pressure and trituration, the alimentary substances were found to have been entirely dissolved. A similar effect takes place when nutritious matters, out of the body, are mixed with the gastric fluid, and the mixture is exposed to a temperature of 100° Fahr. So great, indeed, is the solvent power of this fluid, that it has been known to dissolve the coats of the stomach itself; at least the corrosions of this organ sometimes witnessed in persons who have died suddenly while fasting, and in good health, were ascribed by the celebrated physiologist, John Hunter, to this cause.

No department of chemical physiology is more obscure than that of digestion. There appears so little connection between the properties and composition of the gastric juice, that physiologists are quite at a loss in what way to account for its solvent power. An attempt has lately been made by Tiedemann and Gmelin to explain the phenomena on chemical principles. They ascribe its solvent action to the dilute muriatic and acetic acids, which they maintain to be always secreted during the digestive process, and which, according to their observation, are capable of dissolving most or all of the substances employed as food. They have not shown, however, that the gastric juice in its neutral state, or when neutralized by an alkali, is devoid of solvent properties,

* Philosophical Transactions for 1824.

a circumstance which requires investigation before a decisive opinion can be formed of the accuracy of their views.

## *Bile and Biliary Concretions.*

The bile is a yellow or greenish-yellow coloured fluid, of a peculiar sickening odour, and of a taste at first sweet and then bitter, but exceedingly nauseous. Its consistence is variable, being sometimes limpid, but more commonly viscid and ropy. It is rather denser than water, and may be mixed with that liquid in every proportion. It contains a minute quantity of free soda, and is, therefore, slightly alkaline; but owing to the colour of the bile itself, its action on test paper is scarcely visible.

Of the chemists who have of late years investigated the composition of the bile, Thenard, Berzelius, and Tiedemann and Gmelin deserve particular mention. In an elaborate essay published in the *Memoires d'Arcueil*, vol. i. Thenard endeavoured to show, that the bile of the ox consists of three distinct animal principles, a yellow colouring matter, a species of resin, and a peculiar substance, to which, from its sweetish-bitter taste, he applied the name of *picromel.* According to his analysis, 800 parts of bile consist of water 700 parts, resin 15, picromel 69, yellow matter about 4, soda 4, phosphate of soda 2, muriates of soda and potassa 3.5, sulphate of soda 0.8, phosphate of lime and perhaps magnesia 1.2, and a trace of the oxide of iron. He supposed the resin to be combined with the picromel and soda, and ascribes its solubility in water to this cause.

Berzelius takes a totally different view of the constitution of the bile. He denies that this fluid contains any resinous principle, and regards the yellow matter, resin, and picromel of Thenard, as one and the same substance, to which he applies the name of *biliary matter.* (Medico-Chir. Trans. vol. iii.) Tiedemann and Gmelin, however, in their recent work on digestion, admit the existence of picromel and resin as the chief constituents of bile; although it appears from their experiments that the substance described by Thenard as picromel, was not pure, but contained a portion of resin. According to the analysis of these chemists, the bile of the ox is a very complex fluid, consisting of the following ingredients:—water to the extent of 91.5 per cent; a volatile odoriferous principle; cholesterine; resin; asparagin; picromel; yellow colouring matter; a peculiar azotized substance, soluble in water and alcohol; a substance which is soluble in hot alcohol, but insoluble in water, supposed to be gliadine; osmazome; a principle which emits a urinous odour when heated; a substance analogous to albumen or caseous matter; and mucus. The salts of the bile are the margarate, oleate, acetate, *cholate*, bicarbonate, phosphate, sulphate, and muriate of soda, together with a little phosphate of lime. The *cholic* is a peculiar animal acid, which crystallizes in needles, reddens litmus paper, and is distinguished from analogous compounds by having a sweet taste.

The flaky precipitate which is occasioned by adding acids to bile from the ox, consists of several substances. At first the caseous and colouring matters, along with mucus, are thrown down; and, afterwards, the margaric acid, and a compound of picromel and resin with the acid employed, are precipitated. When acetate of lead is mixed with this fluid, a white precipitate falls, which consists of the oxide of lead combined with the phosphoric, sulphuric, and several other acids, together with a small quantity of the compound of picromel and resin. On adding subacetate of lead to the clear liquid, a copious precipitate

ensues, consisting chiefly of picromel, resin, and oxide of lead. If this compound is suspended in water, through which a current of sulphuretted hydrogen gas is transmitted, the sulphuret of lead and the resin subside, while the picromel remains in solution. By collecting and drying the precipitate, and digesting it in alcohol, the resin is dissolved, and may be obtained by evaporation. The aqueous solution, when evaporated, yields the picromel of Thenard; but according to Tiedemann and Gmelin, it still contains a portion of resin. The chief difficulty, indeed, of preparing pure picromel arises from its tendency to dissolve the resin; and the only mode of separation is by throwing them down repeatedly by means of subacetate of lead. By this process, the affinity of the picromel and resin for each other is gradually lessened, until at length the separation is rendered complete.

Pure picromel occurs in opake rounded crystalline particles, is soluble in water and alcohol, but is insoluble in ether. Its taste is sweet without any bitterness; but it cannot be regarded as a species of sugar, because a large quantity of nitrogen enters into its composition. Its aqueous solution is not precipitated by acids, or by the acetate and subacetate of lead. When digested with the resin of the bile, a portion of the latter is dissolved, and a solution is obtained, which has both a bitter and sweet taste, and yields a precipitate with subacetate of lead and the stronger acids. This is the compound which causes the peculiar taste of the bile.

The bile of the human subject has not been studied so minutely as that of the ox. According to Thenard, it consists, besides salts, of water, colouring matter, albumen, and a species of resin. M. Chevallier has since detected picromel, and M. Chevreul, cholesterine, in human bile; and both these discoveries have been confirmed by the observations of Tiedemann and Gmelin.

The derangement which takes place in the system when the secretion of bile or its passage into the intestines is arrested, is a sufficient indication of the importance of this fluid. It acts as a stimulus to the intestinal canal generally, and produces on the chyme some peculiar change, which is essential to its conversion into chyle.

*Biliary Calculi.*—The concretions which are sometimes formed in the human gall-bladder have been particularly examined by Fourcroy, Thenard, and Chevreul. Fourcroy found that they consist chiefly of a peculiar fatty matter, resembling spermaceti, which he has included under the name of *adipocire* (page 506;) and the experiments of Thenard tended to confirm this view. According to M. Chevreul, however, biliary concretions in general are composed of the yellow colouring matter of the bile and cholesterine, the latter predominating, and being sometimes in a state of purity; and I have had frequent opportunities of satisfying myself of the accuracy of this observation*. These substances may easily be separated from each other by boiling alcohol, which dissolves the cholesterine and leaves the colouring matter; or by digestion in dilute potassa, in which the colouring matter is dissolved, and the cholesterine insoluble.

Gall-stones sometimes contain a portion of inspissated bile; and in some rare instances the cholesterine is entirely wanting.

The concretions found in the gall-bladder of the ox consist almost entirely of the yellow biliary colouring matter, which, from the beauty and permanence of its tint, is much valued by painters. This sub-

* See an interesting case of gall-stone described by Dr Craigie in the Edinburgh Medical and Surgical Journal for 1824.

stance is readily distinguished by its yellow or brown colour, by insolubility in water and alcohol, and by being readily dissolved by a solution of potassa. The solution has at first a yellowish-brown colour, which gradually acquires a green tint, and is precipitated in green flocks by muriatic acid. According to the observation of Tiedemann and Gmelin, the colouring matter is influenced by the presence of oxygen gas. The yellowish precipitate, occasioned by adding muriatic acid to bile, absorbs oxygen by exposure to the air, and its colour changes to green. The action of nitric acid is still more remarkable. By successive additions of this acid, the tint of the colouring matter may be converted into green, blue, violet, and red, in the course of a few seconds.

*Erythrogen.*—This substance was discovered in 1821 by M. Bizio of Venice, in a peculiar fluid, quite different from bile, which was found in the gall-bladder of a person who had died of jaundice. It is of a green colour, transparent, tasteless, and of the odour of putrid fish. It is unctuous to the touch, may be scratched or cut with facility, and has a specific gravity of 1.57. It does not affect the colour of litmus or turmeric paper. At 110° F. it fuses, having the appearance of oil, and crystallizes when slowly cooled; and at 122° F. it rises in the form of vapour. It is insoluble in water and ether, but is dissolved readily by hot alcohol; and the solution, by partial evaporation and cooling, yields crystals in the form of rhomboidal parallelopipedons.

When erythrogen is put into nitric acid of the temperature of about 120° or 140° Fahr. its green tint disappears, effervescence, owing to the escape of oxygen gas, ensues, and the solution acquires a deep purple colour. A similar phenomenon takes place, with disengagement of hydrogen gas, when erythrogen is digested in a solution of ammonia; and when volatilized in the open air, it yields a purple coloured vapour. M. Bizio is of opinion that the erythrogen, under all these circumstances, unites with nitrogen, and that the product is identical with the colouring matter of the blood. The production of the red compound is characteristic of erythrogen, and suggested the name by which this substance is designated (Ερυθρος, *ruber.*) (Journal of Science, vol. xvi.)

Erythrogen has not been discovered either in bile or in any of the animal fluids.

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## SECTION III.

### *CHYLE. MILK. EGGS.*

*Chyle.*—The fluid absorbed by the lacteal vessels from the small intestines during the process of digestion, is known by the name of *chyle*. Its appearance varies in different animals; but as collected from the thoracic duct of a mammiferous animal three or four hours after a meal, it is a white opake fluid like milk, having a sweetish and slightly saline taste. In a few minutes after removal from the duct, it becomes solid, and in the course of twenty-four hours separates into a firm coagulum, and a limpid liquid, which may be called the serum of the chyle. The coagulum is an opake white substance, of a slightly pink hue, insoluble in water, but soluble easily in the alkalies and

alkaline carbonates. Vauquelin* regards it as fibrin in an imperfect state, or as intermediate between that principle and albumen; but Mr Brande† considers it more closely allied to the caseous matter of milk than to fibrin.

The serum of chyle is rendered turbid by heat, and a few flakes of albumen are deposited; but when boiled after being mixed with acetic acid, a copious precipitation ensues. To this substance, which thus differs slightly from albumen, Dr Prout has applied the name of *incipient albumen*. The same chemist has made a comparative analysis of the chyle of two dogs, one of which was fed on animal and the other on vegetable substances, and the result of his inquiry is as follows :—(Annals of Philos. vol. xiii. p. 25.)

| | *Vegetable Food.* | *Animal Food.* |
|---|---|---|
| Water, | 93.6 | 89.2 |
| Fibrin, | 0.6 | 0.8 |
| Incipient albumen? | 4.6 | 4.7 |
| Albumen, with a little red colouring matter, | 0.4 | 4.6 |
| Sugar of milk? | a trace | — |
| Oily matter, | a trace | a trace |
| Saline matters, | 0.8 | 0.7 |
| | 100.0 | 100.0 |

*Milk.*—This well known fluid, secreted by the females of the class *mammalia* for the nourishment of their young, consists of three distinct parts, the cream, curd, and whey, into which by repose it spontaneously separates. The cream, which collects upon its surface, is an unctuous, yellowish-white opake fluid, of an agreeable flavour. According to Berzelius, 100 parts of cream, of specific gravity 1.0244, consist of butter 4.5, caseous matter 3.5, and whey 92. By agitation, as in the process of churning, the butter assumes the solid form, and is thus obtained in a separate state. During the operation there is an increase of temperature amounting to about three or four degrees, oxygen gas is absorbed, and an acid is generated; but the absorption of oxygen cannot be an essential part of the process, since butter may be obtained by churning, even when atmospheric air is entirely excluded.

After the cream has separated spontaneously, the milk soon becomes sour, and gradually separates into a solid coagulum called curd, and a limpid fluid which is whey. This coagulation is occasioned by free acetic acid, and it may be produced at pleasure either by adding a free acid, or by means of the fluid known by the name of *rennet*, which is made by infusing the inner coat of a calf's stomach in hot water. When an acid is employed, the curd is found to contain some of it in combination, and may, therefore, be regarded as an insoluble compound of an acid with the caseous matter of milk; but nothing certain is known respecting the mode by which the gastric fluid, the active principle of rennet, produces its effect.

The curd of skim-milk, made by means of rennet, and separated from the whey by washing with water, is *caseous matter*, or the basis of cheese, in a state of purity. It is a white, insipid, inodorous substance, insoluble in water, but readily soluble in the alkalies, especially in am-

* An. de Ch. vol. xxxi. † Philos. Trans. for 1812.

monia. By alcohol it is converted, like albumen and fibrin, into an adipocirous substance of a fetid odour; and, like the same substances, it may be dissolved by a sufficient quantity of acetic acid.

Caseous matter has considerable analogy to albumen, especially in being coagulated by acids. It is not coagulated, however, by heat; although the tendency to undergo this change is indicated by the film which forms upon the surface of heated milk, an effect apparently connected with exposure to the air. It differs also from albumen in the nature of the spontaneous changes to which it is subject. When kept in a moist state, it undergoes a species of fermentation precisely analogous to that experienced by gluten under the same circumstances. (Page 477.)

The accuracy of the remarks made by Proust concerning the caseous oxide and caseic acid, has been questioned by M. Braconnot. (Edinb. Journal of Science, No. xvi. 369.) The latter states that the curd from spontaneously coagulated skim-milk, covered with water, and kept at a temperature of about 75° F. underwent complete putrefaction in the space of a month. The soluble parts were then filtered, and by evaporation yielded a product of a very fetid odour, acetate of ammonia, and acetic acid. The residue, after being reduced to the consistence of syrup, concreted on cooling into a granulated reddish mass like honey, but of a saline bitter taste, and was separated by the action of alcohol into two parts, one soluble and the other insoluble. The former is the caseate of ammonia of Proust, and the latter, his caseous oxide.

In order to obtain caseous oxide quite pure, it must be washed carefully with alcohol, treated with animal charcoal, and dissolved repeatedly in boiling water, from which it is separated by evaporation. In this state it is a beautiful white powder, inodorous, and of a slight bitter taste. It is heavier than water, and soluble in 14 parts of that fluid at 72° F. On allowing the solution to evaporate spontaneously, it crystallizes either in the form of elegant dendritic ramifications, or in rings composed of delicate acicular crystals of a silky lustre.

Caseous oxide is almost entirely insoluble even in boiling alcohol. Its aqueous solution yields a white flaky precipitate with infusion of gall-nuts, soluble in excess of the precipitant; and subacetate of lead likewise throws down a white precipitate. The crystals, if suddenly heated, volatilize without change; but if the heat is gradually raised, decomposition ensues, and a large quantity of the carbonate and hydrosulphate of ammonia is generated. When strongly heated in open vessels, it takes fire, and burns with flame without residue.

The composition of caseous oxide has not been determined, but from the facility with which its aqueous solution putrefies, M. Braconnot regards it as a highly azotized animal principle. It contains sulphur also. He believes it to be a product of the putrefaction of all animal substances, and proposes for it the name of *aposepedine*, from ἀπὸ and σηπεδὼν, result of putrefaction, as more appropriate than caseous oxide.

M. Braconnot denies the existence of caseic acid. Proust's caseate of ammonia consists of various substances, such as free acetic acid, aposepedine, animal matter, resin, several salts, and a yellow pungent oil, which is the chief cause of the pungency of old cheese.

From 750 parts of curd completely putrefied were obtained 36 of dry matter insoluble in water. These consisted of 14.92 parts of margarate of lime, 2.57 of margaric acid, and 18.51 of oleic acid, retaining margaric acid and a brown animal matter.

According to the analysis of Gay-Lussac and Thenard, 100 parts of

the caseous matter are composed of carbon 59.781, hydrogen 7.429, oxygen 11.409, and nitrogen 21.381. It yields by incineration a white ash, amounting to 6.5 per cent of its weight, the greater part of which is phosphate of lime, a circumstance which renders caseous matter an article of food peculiarly proper for young animals.

Milk carefully deprived of its cream has a specific gravity of about 1.033; and 1000 parts of it, according to Berzelius, are thus constituted;—water 928.75; caseous matter with a trace of butter 28; sugar of milk 35; muriate and phosphate of potassa 1.95; lactic (acetic) acid, acetate of potassa, and a trace of lactate of iron 6; and earthy phosphates 0.30. Subtracting the caseous matter, the remaining substances constitute whey.

*Eggs.*—The composition of the recent egg and the changes which it undergoes during the process of incubation, have been ably investigated by Dr Prout. (Phil. Trans. for 1822.) New-laid eggs are rather heavier than water; but they become lighter after a time, in consequence of water evaporating through the pores of the shell, and air being substituted for it. An egg of ordinary size yields to boiling water about three-tenths of a grain of saline matter, consisting of the sulphates, carbonates, and phosphates of lime and magnesia, together with animal matter and a little free alkali.

Of an egg which weighs 1000 grains, the shell constitutes 106.9, the white 604.2, and the yelk 288.9 grains. The shell contains about two per cent of animal matter, one per cent of the phosphates of lime and magnesia, and the residue is carbonate of lime with a little carbonate of magnesia.

When the yelk of a hard boiled egg is repeatedly digested in alcohol of specific gravity 0.807, until that fluid comes off colourless, there remains a white pulverulent residuum, possessed of many of the properties of albumen, but distinguished from that principle by containing a large quantity of phosphorus in some unknown state of combination. The alcoholic solution is of a deep yellow colour, and on cooling deposites crystals of a sebaceous matter, and a portion of yellow semifluid oil. On distilling off the alcohol, the oil is left in a separate state. When the yelk is dried and burned, the phosphorus is converted into phosphoric acid, which, melting into a glass upon the surface of the charcoal, protects it from complete combustion. In the white of the egg, which consists chiefly of albumen, sulphur is present.

The obvious use of the phosphorus contained in the yelk is to supply phosphoric acid for forming the bones of the chick; but Dr Prout was unable to discover any source of the lime, with which that acid unites to form the earthy part of bone. It cannot be discovered in the soft parts of the egg; and hitherto no vascular connection has been traced between the chick and its shell.

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## SECTION IV.

### *ON THE LIQUIDS OF SEROUS AND MUCOUS SURFACES, &c. AND ON PURULENT MATTER.*

The surface of the cellular membrane is moistened with a peculiar limpid transparent fluid called *lymph,* which is in very small quantity

during health, but collects abundantly in some dropsical affections. Mr Brande collected it from the thoracic duct of an animal which had been kept without food for twenty-four hours. Its chief constituent is water, besides which it contains muriate of soda and albumen, the latter being in such minute quantity that it is coagulated only by the action of galvanism. Lymph does not affect the colour of test paper; but when evaporated to dryness, the residue gives a green tint to the syrup of violets.

The fluid secreted by the serous membranes in general, such as the pericardium, pleura, and peritoneum, is very similar to lymph. According to Dr Bostock, 100 parts of the liquid of the pericardium consist of water 92 parts, albumen 5.5, mucus 2, muriate of soda 0.5. The serous fluid exhaled within the ventricles of the brain in *hydrocephalus internus* is composed, in 1000 parts, of water 988.3, albumen 1.66, muriate of potassa and soda 7.09, lactate (acetate) of soda and its animal matter 2.32, soda 0.28, and animal matter soluble only in water, with a trace of phosphates, 0.35. (Berzelius, in Medico-Chir. Trans. vol. iii. p. 252.)

The liquor of the amnios, or the fluid contained in the membrane which surrounds the *fœtus in utero*, differs in different animals. That of the human female was found by Vauquelin and Buniva to contain a small quantity of albumen, soda, muriate of soda, phosphate and carbonate of lime, and a matter like curd, which gives it a milky appearance. That of the cow, according to the same authority, contains the substance already described under the name of amniotic acid; but several other chemists, such as Prout, Dulong and Labillardière, and Lassaigne have been unable to detect it. M. Lassaigne states, that this acid exists in the fluid of the allantois of the cow. Dr Prout found some sugar of milk in the amnios of a woman. (Ann. of Phil. vol. v. p. 417.)

*Humours of the Eye.*—The aqueous and vitreous humours of the eye contain rather more than 80 per cent of water. The other constituents are a small quantity of albumen, muriate and acetate of soda, pure soda, though scarcely sufficient to affect the colour of test paper, and animal matter soluble only in water, but which is not gelatin. (Berzelius.) The crystalline lens, besides the usual salts, contains 36 per cent of a peculiar animal matter, very analogous to albumen if not identical with it. In cold water it is soluble, but is coagulated by boiling. The coagulum, according to Berzelius, has all the properties of the colouring matter of the blood excepting its colour.

The tears are limpid and of a saline taste, dissolve freely in water, and, owing to the presence of free soda, communicate a green tint to the blue infusion of violets. Their chief salts are the muriate and phosphate of soda. According to Fourcroy and Vauquelin, the animal matter of the tears is mucus; but it is more probably either albumen, or some analogous principle. Its precise nature has not however been satisfactorily determined.

*Mucus.*—The term *mucus* has been employed in very different significations. Dr Bostock applies it to a peculiar animal matter which is soluble both in hot and cold water, is not precipitated by corrosive sublimate or solution of tannin, is not capable of forming a jelly, and which yields a precipitate with subacetate of lead.

The existence of this principle has not, however, been fully established; for the presence of muriatic and phosphoric acids, the latter of which is frequently contained in animal fluids, and the former scarcely ever absent, sufficiently accounts for the precipitates occasioned in them by the salts of lead or silver. But even supposing the opinion

of Dr Bostock to be correct, it would be advisable to give some new name to his principle, and apply the term mucus solely to the fluid secreted by mucous surfaces.

The properties of mucus vary somewhat according to the source from which it is derived; but its leading characters are in all cases the same, and are best exemplified in mucus from the nostrils. Nasal mucus, according to Berzelius, has the following properties. Immersed in water, it imbibes so much of that fluid as to become transparent, with the exception of a few particles which remain opake. When dried on blotting paper, it loses its transparency, but again acquires it when moistened. It is not coagulated or rendered horny by being boiled in water; but as soon as the ebullition has ceased, it collects unchanged at the bottom of the vessel. It is dissolved by dilute sulphuric acid. Nitric acid at first coagulates it; but by continued digestion, the mucus at first softens and is finally dissolved, forming a clear yellow liquid. Acetic acid hardens mucus, and does not dissolve it even at a boiling temperature. Pure potassa at first renders it more viscid, but afterwards dissolves it. By tannin, mucus is coagulated, both when softened by the absorption of water, and when dissolved either in an acid or an alkali.

*Pus.*—Purulent matter is the fluid secreted by an inflamed and ulcerated surface. Its properties vary according to the nature of the sore from which it is discharged. The purulent matter formed by an ill-conditioned ulcer is a thin, transparent, acrid, fetid ichor; whereas a healing sore in a sound constitution yields a yellowish-white coloured liquid, of the consistence of cream, which is described as bland, opake, and inodorous. This is termed healthy pus, and is possessed of the following properties. Though it appears homogeneous to the naked eye, when examined with the microscope, it is found to consist of minute globules floating in a transparent liquid. Its specific gravity is about 1.03. It is insoluble in water; and is thickened, but not dissolved by alcohol. When recent it does not affect the colour of test paper; but by exposure to the air, it becomes acid. The dilute acids have little effect upon it; but strong sulphuric, nitric, and muriatic acids dissolve it, and the pus is thrown down by dilution with water. Ammonia reduces it to a transparent jelly, and gradually dissolves a considerable portion of it. With the fixed alkalies, it forms a whitish ropy fluid, which is decomposed by water.

The composition of pus has not been ascertained with precision; but its characteristic ingredient is more closely allied to albumen than the other animal principles.

Several attempts have been made to discover a chemical test for distinguishing pus from mucus. When these fluids are in their natural state, the appearance of each is so characteristic that the distinction cannot be attended with any difficulty; but, on the contrary, when a mucous surface is inflamed, its secretion becomes opake, and, as sometimes happens in some pulmonary diseases, acquires more or less of the aspect of pus. Mr Charles Darwin, who examined this subject, pointed out three grounds of distinction between them. 1. When the solution of these liquids in sulphuric acid is diluted, the pus subsides to the bottom, and the mucus remains suspended in the water. 2. When pus and catarrhal mucus are diffused through water, the former sinks, and the latter floats. 3. Pus is precipitated from its solution in potassa by water, while the solution of mucus is not decomposed by similar treatment. Dr Thomson, in his system of chemistry, has given the following test on the authority of Grassmeyer. The substance to be examined, after being tri turated with its own weight

of water, is mixed with an equal quantity of a saturated solution of the carbonate of potassa. If it contain pus, a transparent jelly forms in a few hours; but this does not happen if mucus only is present. Dr Young, in his work on Consumptive Diseases, has given a very elegant character for distinguishing pus, founded on its optical properties. But the practical utility of tests of any kind is rendered very questionable by the fact, that inflamed mucous membranes may secrete genuine pus without breach of surface, and that the natural passes into purulent secretion by insensible shades.

*Sweat.*—Watery vapour is continually passing off by the skin in the form of insensible perspiration; but when the external heat is considerable, or violent bodily exercise is taken, drops of fluid collect upon the surface, and constitute what is called sweat. This fluid consists chiefly of water; but it contains some muriate of soda and free acetic acid, in consequence of which it has a saline taste and an acid reaction.

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## SECTION V.

### *ON THE URINE AND URINARY CONCRETIONS.*

The urine differs from most of the animal fluids which have been described by not serving any ulterior purpose in the animal economy. It is merely an excretion designed for ejecting from the system substances, which, by their accumulation within the body, would speedily prove fatal to health and life. The sole office of the kidneys, indeed, appears to consist in separating from the blood the superfluous matters that are not required or adapted for nutrition, or which have already formed part of the body, and been removed by absorption. The substances which in particular pass off by this organ are nitrogen, in the form of highly azotized products, and various saline and earthy compounds. This sufficiently accounts for the great diversity of different substances contained in the urine.

The quantity of the urine is affected by various causes, especially by the nature and quantity of the liquids received into the stomach; but on an average a healthy person voids between thirty and forty ounces daily. The quality of this fluid is likewise influenced by the same circumstances, being sometimes in a very dilute state, and at others highly concentrated. The urine voided in the morning by a person who has fed heartily, and taken no more fluids than is sufficient for satisfying thirst, may be regarded as affording the best specimen of natural healthy urine.

The urine in this state is a transparent limpid fluid of an amber colour, having a saline taste, and while warm emitting an odour which is slightly aromatic, and not at all disagreeable. Its specific gravity in its most concentrated form, is about 1.030. It gives a red tint to litmus paper, a circumstance which indicates the presence either of a free acid or of a super-salt. Though at first quite transparent, an insoluble matter is deposited on standing; so that urine, voided at night is found to have a light cloud floating in it by the following morning. This substance consists in part of mucus from the urinary passages, and partly of the superurate of ammonia, which is much more soluble in warm than in cold water.

The urine is very prone to spontaneous decomposition. When

kept for two or three days, it acquires a strong urinous smell; and as the putrefaction proceeds, the disagreeable odour increases, until at length it becomes exceedingly offensive. As soon as these changes commence, the urine ceases to have an acid reaction, and the earthy phosphates are deposited. In a short time, a free alkali makes its appearance, and a large quantity of carbonate of ammonia is gradually generated. Similar changes may be produced in recent urine by continued boiling. In both cases the phenomena are owing to the decomposition of urea, which is almost entirely resolved into carbonate of ammonia.

The composition of the urine has been studied by several chemists, but the most recent and elaborate analysis of this fluid is by Berzelius. According to the researches of this indefatigable chemist, 1000 parts of urine are composed of

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|---|---|
| Water, | 933.00 |
| Urea, | 30.10 |
| Uric acid, | 1.00 |
| Free lactic acid, lactate of ammonia, and animal matter not separable from them, | 17.14 |
| Mucus of the bladder, | 0.32 |
| Sulphate of potassa, | 3.71 |
| Sulphate of soda, | 3.16 |
| Phosphate of soda, | 2.94 |
| Phosphate of ammonia, | 1.65 |
| Muriate of soda, | 4.45 |
| Muriate of ammonia, | 1.50 |
| Earthy matters, with a trace of fluate of lime, | 1.00 |
| Siliceous earth, | 0.03 |

Besides the ingredients included in the preceding list, the urine contains several other substances in small quantity. From the property this fluid possesses of blackening silver vessels in which it is evaporated, owing to the formation of the sulphuret of silver, Proust inferred the presence of unoxidized sulphur; and Dr Prout, from the odour of phosphuretted hydrogen, which he thinks he has perceived in putrefying urine, suspects that phosphorus is likewise present. The urine also contains a peculiar yellow colouring matter, which has not hitherto been obtained in a separate state. From the precipitate occasioned in urine by the infusion of gall-nuts, the presence of gelatin has been inferred; but this effect appears owing to the presence not of gelatin but of a small portion of albumen.

According to Scheele, the urine of infants sometimes contains benzoic acid, a compound which, when present, may be easily procured by evaporating the urine nearly to the consistence of syrup, and adding muriatic acid. The precipitate, consisting of uric and benzoic acids, is digested in alcohol, which dissolves the benzoic acid.

Notwithstanding the high authority of Berzelius, it is very doubtful if any free acid be present in healthy urine. Dr Prout, with every appearance of justice, maintains that the acidity of recent urine is occasioned by super-salts, and not by uncombined acid. He is of opinion that the acid reaction is chiefly, if not wholly, to be ascribed to the superphosphate of lime and superurate of ammonia, salts which he finds may co-exist in a liquid without mutual decomposition. A very strong argument, which to me indeed appears conclusive in favour of this view, is derived from the fact, that on adding muriatic acid to recent urine, minute crystals of uric acid are gradually deposit-

ed, as always happens when this acid subsides slowly from a state of solution; but, on the contrary, if no free acid is added, an amorphous sediment, which Dr Prout regards as the superurate of ammonia, is obtained.

Such is a general view of the composition of human urine in its natural healthy state. But this fluid is subject to a great variety of morbid conditions, which arise either from the deficiency or excess of certain principles which it ought to contain, or from the presence of others wholly foreign to its composition. As the study of these affections affords an interesting example of the application of chemistry to pathology and the practice of medicine, I shall mention briefly some of the most important morbid states of this fluid, referring for more ample details to the excellent treatise of Dr Prout*.

Of the substances which, though naturally wanting, are sometimes contained in the urine, the most remarkable is sugar, which is secreted by the kidneys in diabetes. (Page 500.) Diabetic urine has a sweet taste, and yields a syrup by evaporation, is almost always of a pale straw colour, and in general has a greater specific gravity than ordinary urine. It contains a remarkably small proportion of azotized substances, so that it has no tendency to putrefy; but the presence of sugar renders it susceptible of undergoing the vinous fermentation.

The acidifying process which is constantly going forward in the kidneys, as evinced by the formation of sulphuric, phosphoric, and uric acids, sometimes proceeds to a morbid extent, in consequence of which two acids, the oxalic and nitric, are generated, neither of which exists in healthy urine. The former, by uniting with lime gives rise to one of the worst kinds of urinary concretions; and the latter, in the opinion of Dr Prout, leads to the production of the purpurate of ammonia, by reacting on uric acid.

In severe cases of jaundice, the bile passes from the blood into the kidneys, and communicates a yellow colour to the urine. The most delicate test of its presence is muriatic acid, which causes a green tint.

Though albumen is contained in very minute quantity in healthy urine, in some diseases it is present in large proportion. According to Dr Blackall, it is characteristic of certain kinds of dropsy, accompanied with an inflammatory diathesis, as in that which supervenes on scarlet fever; and Dr Prout has described two cases of albuminous urine, in which, without any febrile symptoms, albumen existed in such quantity that spontaneous coagulation took place within the bladder. From the Medical Reports lately published by Dr Bright, it appears that dropsical effusions are sometimes owing to an inflammatory or diseased state of the kidneys; and in these cases the urine commonly contains so much albumen as to be rendered turbid by heat. So regular indeed is its occurrence, that Dr Bright considers albuminous urine, in dropsical patients, to be a sign of renal disease.

In certain states of the system, urea is generated in an unusually small proportion. This occurs especially in *diabetes mellitus*, and in acute and chronic inflammation of the liver, diseases in which urea is said sometimes to be wholly wanting; but the experience of Dr Prout has led him to doubt if it is ever entirely absent. Dr Henry has shown that urea, when mixed with a considerable proportion of sugar, cannot be discovered by the usual test of nitric acid; and, consequently, that though present in diabetic urine, it may easily be overlooked. The method by which he has succeeded in detecting it in such cases is by

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* Inquiry into the Nature and Treatment of Gravel, Calculus, &c.

distillation, urea being the only known animal principle which is converted into carbonate of ammonia at a boiling temperature. (Medico-Chir. Trans. vol. ii. p. 127.) During the hysteric paroxysm, also, the animal matters of the urine are deficient, while its saline ingredients are secreted in unusual quantity. An excess of urea occasionally exists. The mode by which Dr Prout estimates the proportion of this principle is by putting the urine in a watch glass, and carefully adding to it nearly an equal quantity of nitric acid, in such a manner that the acid may collect at the bottom. If spontaneous crystallization ensue, an excess of urea is indicated; and the degree of excess may be inferred approximately by marking the time which elapses before the effect takes place. Undiluted healthy urine yields crystals only after an interval of half an hour; but the nitrate crystallizes within that interval when the urea is in excess.

An unusually abundant secretion of uric acid is a circumstance by no means uncommon. In some instances this acid makes it appearance in a free state; but happily it generally occurs in combination with an alkali, especially with soda or ammonia. As the urates are much more soluble in warm than in cold water, the urine in which they abound is quite clear at the moment of being voided, but deposites a copious sediment in cooling. The undue secretion of these salts, if temporary, occasions scarcely any inconvenience, and arises from such slight causes, that it frequently takes place without being noticed. This affection is generally produced by errors in diet, whether as to quantity or quality, and by all causes which interrupt the digestive process in any of its stages, or render it imperfect. Dr Prout specifies unfermented heavy bread, and hard boiled puddings or dumplings, as in particular disposing to the formation of the urates. These sediments have commonly a yellowish tint, which is communicated by the colouring matter of the urine; or when they are deposited in fevers, forming the lateritious sediment, they are red, in consequence of the colouring matter of the urine being then more abundant. In fevers of an irritable nature, as in hectic, the sediment has a pink colour, which is ascribed by Dr Prout to the presence of purpurate of ammonia, and by Proust to rosacic acid. (Page 502.)

So long as the uric acid remains in combination with a base, it never yields a crystalline deposite; but when this acid is in excess and in a free state, its very sparing solubility causes it to separate in minute crystals, even within the bladder, giving rise to two of the most distressing complaints to which human nature is subject,—to gravel when the crystals are detached from one another, and when agglutinated by animal matter into concrete masses, to the disease called stone. These diseases may arise either from uric acid being directly secreted by the kidneys, or, as Dr Prout suspects, from the formation of some other acid, by which the urate of ammonia is decomposed. The tendency of the urine to contain free acid occurs most frequently in dyspeptic persons of a gouty habit, and is familiarly known by the name of the uric or lithic acid diathesis. In these individuals, the disposition to undue acidity of the urine is superadded to that state of the system which leads to an unusual supply of the urates.

A deficiency of acid in the urine is not less injurious than its excess. As the phosphate of lime in its neutral state is insoluble in water, this salt cannot be dissolved in the urine, except by being in the form of a superphosphate. Hence it happens that healthy urine yields a precipitate, when it is neutralized by an alkali; and if, by the indiscriminate employment of alkaline medicines, or from any other cause, the urine, while yet within the bladder, is rendered neutral, the earthy phos-

phates are necessarily deposited, and an opportunity afforded for the formation of a stone.

## *Urinary Concretions.*

The first step towards a knowledge of urinary calculi was made in the year 1776 by Scheele, who showed that many of the concretions formed in the bladder consist of uric or lithic acid. The subject was afterwards successfully investigated by Drs Wollaston and Pearson in this country, and by Fourcroy and Vauquelin in France; but the honour of having first ascertained the composition and chemical characters of most of the species of urinary calculi at present known, belongs to Dr Wollaston. (Phil. Trans. for 1797.) The chemists who have since materially contributed to advance our knowledge of this department of science, are Dr Henry, Mr Brande, Dr Prout, and the late Dr Marcet, to whose "Essay on the Chemical History and Medical Treatment of Calculous Disorders," I may refer the reader who is desirous of studying this important subject.

The most common kinds of urinary concretions may be conveniently divided into six species: 1. The uric acid calculus; 2. The bone-earth calculus, principally consisting of phosphate of lime; 3. The ammoniaco-magnesian phosphate; 4. The fusible calculus, being a mixture of the two preceding species; 5. The mulberry calculus, composed of oxalate of lime; and, lastly, The cystic oxide calculus. (Marcet.)

1. The uric acid forms a hard inodorous concretion, commonly of an oval form, of a brownish or fawn colour, and smooth surface. These calculi consist of layers arranged concentrically around a central nucleus, the laminæ being distinguished from each other by a slight difference in colour, and sometimes by the interposition of some other substance.

This species is readily distinguished by the following characters. It is very sparingly soluble in water and muriatic acid. Digested in pure potassa it quickly disappears, and on adding an acid to the solution, the uric acid is precipitated. It is dissolved with effervescence by nitric acid, and the solution yields the purpurate of ammonia when evaporated. Before the blowpipe, it becomes black, emits a peculiar animal odour, and is gradually consumed, leaving a trace of white ash, which has an alkaline reaction.

As a variety of this species, may be mentioned the urate of ammonia, a rare kind of calculus first noticed by Fourcroy. Mr Brande and Dr Marcet expressed a doubt of its ever forming an independent concretion; but its existence, as such, has been established by Dr Prout. The urate of ammonia has the same general chemical characters as the uric acid, from which it is distinguished by its solubility in boiling water, when reduced to powder, and by its solution in potassa being attended with the disengagement of ammonia. It deflagrates remarkably before the blowpipe. (Medico-Chir. Trans. vol. x. p. 389.)

2. The bone-earth calculus, first correctly analyzed by Dr Wollaston, consists of phosphate of lime. The surface of these calculi is of a pale brown colour, and quite smooth as if they had been polished. When sawed through the middle, they are found to be laminated in a very regular manner, and the layers in general adhere so slightly that they may be separated with ease into concentric crusts.

This calculus, when reduced to powder, dissolves with facility in dilute nitric or muriatic acid, but is insoluble in potassa. Before the blowpipe, it first assumes a black colour, from the decomposition of a

little animal matter, and then becomes quite white, undergoing no further change unless the heat be very intense, when it is fused.

3. The phosphate of ammonia and magnesia was first described as a constituent of urinary calculi by Dr Wollaston. It rarely exists quite alone, because the same state of the urine which leads to the formation of this species, favours the deposition of phosphate of lime; but it is frequently the prevailing ingredient. It often appears in the form of minute sparkling crystals, diffused over the surface or between the interstices of other calculus laminæ.

Calculi, in which this salt prevails, are generally white, and less compact than the foregoing species. When reduced to powder they are dissolved by cold acetic acid, and still more easily by the stronger acids, the salt being thrown down unchanged by ammonia. Digested in pure potassa, it emits an ammoniacal odour, but it is not dissolved. Before the blowpipe, a smell of ammonia is given out, it diminishes in size, and melts into a white pearl with rather more facility than phosphate of lime.

4. The fusible calculus, the nature of which was first determined by Dr Wollaston, is a mixture of the two preceding species. It is commonly of a white colour, and its fracture is usually ragged and uneven. It is more friable than any of the other kinds of calculus, separates easily into layers, and leaves a white dust on the fingers. These concretions are very common, and sometimes attain a large size.

The fusible calculus is characterized by the facility with which it melts into a pearly globule, which is sometimes quite transparent. When reduced to powder, and put into cold acetic acid, the phosphate of ammonia and magnesia is dissolved, and the phosphate of lime, almost the whole of which is left, dissolves readily in muriatic acid.

5. The mulberry calculus, so named from its resemblance to the fruit of the mulberry, was first proved to consist of oxalate of lime by Dr Wollaston. This concretion is sufficiently characterized by its dark coloured tuberculated surface; but it may also be distinguished chemically by the following properties. Heated before the blowpipe, the oxalic acid is decomposed, and pure lime remains, which gives a strong brown stain to moistened turmeric paper. It is insoluble in the alkalies; but by digestion in carbonate of potassa it is decomposed, and the insoluble carbonate of lime is left. When reduced to powder and digested in muriatic or nitric acid, a perfect solution is effected. It is not dissolved by acetic acid, a circumstance which distinguishes it from the ammoniaco-magnesian phosphate; and it is distinguished from phosphate of lime by being insoluble in phosphoric acid.

6. The cystic oxide was described by its discoverer Dr Wollaston in the Philosophical Transactions for 1810. This concretion is not laminated, but appears as one uniform mass, confusedly crystallized through its whole substance, having somewhat the appearance of the ammoniaco-magnesian phosphate, though more compact. Before the blowpipe, it emits a peculiarly fetid smell, quite distinct from that of uric acid, and is consumed. It is characterized by the great variety of reagents in which it is soluble. It is dissolved abundantly by the muriatic, nitric, sulphuric, and oxalic acids; by potassa, soda, ammonia, and lime-water; and even by the neutral carbonates of soda and potassa. It is insoluble in water, alcohol, bicarbonate of ammonia, and in the tartaric, citric, and acetic acids.

From the similarity which this substance bears to certain oxides in uniting both with acids and alkalies, Dr Wollaston termed it an oxide,

and gave it the name of *cystic*, on the supposition of its being peculiar to the bladder. Dr Marcet, however, has found it in the kidney.

The cystic oxide is a rare species of calculus. In this country seven specimens only have been found;—two by Dr Wollaston, two by Dr Henry, and three by Dr Marcet. Professor Stromeyer has met with two instances of it in one family, and in one of the cases the cystic oxide was also detected in the urine. M. Lassaigne has likewise found it in a stone taken from the bladder of a dog. From the analysis of this chemist, 100 parts of cystic oxide are composed of carbon 36.2, hydrogen 12.8, oxygen 17, and nitrogen 34.

It is remarkable that cystic oxide is never accompanied with the matter of any other concretion; whereas the other species are frequently met with in the same stone. They are sometimes so intimately mixed that they can be separated from one another only by chemical analysis, forming what is called a *compound* calculus; but more frequently the concretion consists of two or more different species arranged in distinct alternate layers. This is termed the *alternating* calculus.

Besides the calculi just mentioned, three other species have been noticed. Two of these were described by Dr Marcet under the names of *xanthic oxide* and *fibrinous calculus*, both of which are exceedingly rare. The xanthic oxide is of a reddish or yellow colour, is soluble both in acids and alkalies, and its solution in nitric acid, when evaporated, assumes a bright lemon-yellow tint, a property to which it owes its name, and by which it is characterized. (ξανθος yellow.) The fibrinous calculus derives its name from fibrin, to which its properties are closely analogous. The third species consists chiefly of carbonate of lime, and is likewise of rare occurrence.

From the solubility of urinary concretions in chemical menstrua, hopes were once entertained that reagents might be introduced into the urine through the medium of the blood, or be at once injected into the bladder, so as to dissolve urinary calculi, and thus supersede the necessity of a painful operation which is not void of danger. It has been found, however, that, for this purpose, it would be necessary to employ acid or alkaline solutions of greater strength than may safely be introduced into the bladder, and consequently all attempts of the kind have been abandoned. The last suggestion of this nature was made by Messrs Prevost and Dumas, who propose to disunite the elements of calculi by means of galvanism. This agent, however, though it may produce this effect out of the body, will scarcely, I conceive, be found admissible in practice.

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# SECTION VI.

## *ON THE SOLID PARTS OF ANIMALS.*

## *Bones, Horn, Membranes, Tendons, Ligaments, Muscle, &c.*

Bones consist of earthy salts and animal matter intimately blended, the former of which are designed for giving solidity and hardness, and

the latter for agglutinating the earthy particles. The animal substances are chiefly cartilage, gelatin, and a peculiar fatty matter called marrow. On reducing bones to powder, and digesting them in water, the fat rises and swims upon its surface, while the gelatin is dissolved. By digesting bones in dilute muriatic acid, both the gelatin and earthy salts are dissolved, and the pure cartilage is left, which is flexible, but retains the original figure of the bone. The cartilage of bones is formed before the earthy matter, and constitutes the nidus in which the latter is deposited. In its chemical properties, it is very analogous to coagulated albumen.

When bones are heated in close vessels, a large quantity of carbonate of ammonia, some fetid empyreumatic oil, and the usual inflammable gases pass over into the recipient; while a mixture of charcoal and earthy matter, called animal charcoal, remains in the retort. If, on the contrary, they are heated to redness in an open fire, the charcoal is consumed, and a pure white friable earth is the sole residue.

According to the analysis of Berzelius, 100 parts of dry human bones consist of animal matters 33.3, phosphate of lime 51.04, carbonate of lime 11.30, fluate of lime 2, phosphate of magnesia 1.16, and soda, muriate of soda, and water 1.2. Mr Hatchett found, also, a small quantity of sulphate of lime; and Fourcroy and Vauquelin discovered traces of alumina, silica, and the oxides of iron and manganese.

Teeth are composed of the same materials as bone; but the enamel dissolves completely in dilute nitric acid, and therefore is free from cartilage. From the analysis of Mr Pepys, the enamel contains 78 per cent of phosphate, and 6 of carbonate of lime, the residue being probably gelatin. The composition of ivory is similar to that of the bony matter of teeth in general.

The shells of eggs and the covering of crustaceous animals, such as lobsters, crabs, and the starfish, consist of the carbonate and a little phosphate of lime, and animal matter. The shells of oysters, muscles, and other molluscous animals consist almost entirely of carbonate of lime and animal matter, and the composition of pearl and mother of pearl is similar.

Horn differs from bone in containing only a trace of earth. It consists chiefly of gelatin and a cartilaginous substance like coagulated albumen. The composition of the nails and hoofs of animals is similar to that of horn; and the cuticle belongs to the same class of substances.

Tendons appear to be composed almost entirely of gelatin; for they are soluble in boiling water, and the solution yields an abundant jelly on cooling. The composition of the true skin is nearly the same as that of tendons. Membranes and ligaments are composed chiefly of gelatin, but they also contain some substance which is insoluble in water, and is similar to coagulated albumen.

According to the analysis of Vauquelin, the principal ingredient of hair is a peculiar animal substance, insoluble in water at 212° F. but which may be dissolved in that liquid by means of Papin's digester, and is soluble in a solution of potassa. Besides this substance, hair contains oil, sulphur, silica, iron, manganese, and the carbonate and phosphate of lime. The colour of the hair depends on that of its oil; and the effect of metallic solutions, such as nitrate of silver, in staining the hair, is owing to the presence of sulphur.

The composition of wool and feathers appears analogous to that of hair. The quill part of the feather was found by Mr Hatchett to consist of coagulated albumen.

Silk is covered with a peculiar varnish which is soluble in boiling water and in alkaline solutions, and amounts to about 23 per cent of the raw material. By digestion in alcohol it is also deprived of a portion of wax. The remaining fibrous structure has been examined in a very imperfect manner. By the action of nitric acid, it is converted into a yellow crystalline substance of a bitter taste.

The flesh of animals, or *muscle*, consists essentially of fibrin; but independently of this principle, it contains several other ingredients, such as albumen, gelatin, a peculiar extractive matter called *osmazome*, fat, and salts; substances which are chiefly derived from the blood, vessels, and cellular membrane, dispersed through the muscles. On macerating flesh, cut into small fragments, in successive portions of cold water, the albumen, osmazome, and salts are dissolved; and on boiling the solution, the albumen is coagulated. From the remaining liquid, the osmazome may be procured in a separate state by evaporating to the consistence of an extract, and treating it with cold alcohol. By the action of boiling water, the gelatin of the muscle is dissolved, the fat melts and rises to the surface of the water, and pure fibrin remains.

The characteristic odour and taste of soup are owing to the osmazome. This substance is of a yellowish-brown colour, and is distinguished from the other animal principles by solubility in water and alcohol, whether cold or at a boiling temperature, and by not forming a jelly when its solution is concentrated by evaporation. Like gelatin and albumen, it yields a precipitate with infusion of nut-galls.

The substance of the brain, nerves, and spinal marrow differs from that of all other animal textures. The most elaborate analysis of cerebral matter is by Vauquelin, who found that 100 parts of it consist of water 80, albumen 7, white fatty matter 4.53, red fatty matter 0.70, osmazome 1.12, phosphorus 1.5, and acids, salts, and sulphur 5.15. (Annals of Phil. vol. i.) The presence of albumen accounts for the partial solubility of the brain in cold water, and for the solution being coagulated by heat, acids, alcohol, and by the metallic salts which coagulate other albuminous fluids. By acting upon cerebral matter with boiling alcohol, the fatty principles and osmazome are dissolved, and the solution in cooling deposites the white fatty matter in the form of crystalline plates. On expelling the alcohol by evaporation, and treating the residue with cold alcohol, the osmazome is taken up, and a fixed oil remains of a reddish-brown colour, and an odour like that of the brain itself, though much stronger. These two species of fat differ little from each other, and both yield phosphoric acid when deflagrated with nitre.

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## SECTION VII.

### *ON PUTREFACTION.*

When dead animal matter is exposed to air, moisture, and a moderate temperature, it speedily runs into putrefaction, during which every trace of its original texture disappears, and products of a very offensive nature are generated. The presence of air, by affording oxygen, accelerates the change; but the conditions which may be regarded as essential to it, are moisture and a certain temperature, causes which

operate in the same manner as in the putrefaction of vegetable matter. The most favourable temperature is from 60° to 80° or 90° Fahr. Below 50° the process takes place tardily, and at 32° it is wholly arrested;—a fact, which is clearly evinced by the circumstance that the bodies of animals, which have been buried in snow or ice, are found unchanged after a long series of years. The necessity of a certain degree of moisture is shown by the facility with which the most perishable substances may be preserved when quite dry. The preservation of smoked meat is chiefly owing to this cause; and, for a like reason, animals buried in the dry sand of Arabia and Egypt have remained for years without change.

For reasons formerly mentioned, animal matters commonly undergo putrefaction more readily than those which are derived from the vegetable kingdom, (page 423); but they are not all equally disposed to putrefy. The acid and fatty principles are less liable to this change than urea, fibrin, and other analogous substances. The chief products to which their dissolution gives rise are water, ammonia, carbonic acid, and sulphuretted, phosphuretted, and carburetted hydrogen gases.

# PART IV.

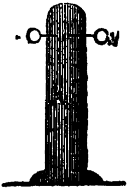
## ANALYTICAL CHEMISTRY.

TO enter into a detailed account of experimental and analytical chemistry, is altogether inconsistent with the design and limits of the present work. My sole object in this department is to give a few concise directions for conducting some of the more common analytical processes; and in order to render them more generally useful, I shall give examples of the analysis of mixed gases, of minerals, and of mineral waters.

# SECTION I.

## ANALYSIS OF MIXED GASES.

*Analysis of Air or of Gaseous Mixtures containing Oxygen.*—Of the various processes by which oxygen gas may be withdrawn from gaseous mixtures, and its quantity determined, none are so convenient and precise as the method by means of hydrogen gas. In performing this analysis, a portion of atmospheric air is carefully measured in a graduated tube, and mixed with a quantity of hydrogen gas which is rather more than sufficient for uniting with all the oxygen present. The mixture is then introduced into a strong glass tube called Volta's eudiometer, shown in the annexed wood-cut, and is inflamed by the electric spark, the aperture of the tube being closed by the thumb at the moment of detonation. The total diminution in volume, divided by three, indicates the quantity of oxygen originally contained in the mixture. This operation may be performed in a trough either of water or mercury.

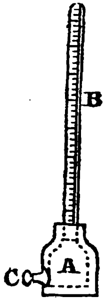


Instead of electricity, spongy platinum may be employed for causing the union of oxygen and hydrogen gases; and while its indications are very precise, it has the advantage of producing the effect gradually and without detonation. The most convenient mode of employing it with this intention is the following. A mixture of spongy platinum and pipe-clay, in the proportion of about three parts of the former to one of the latter, is made into a paste with water, and then rolled between the fingers into a globular form. In order to preserve the spongy texture of the platinum, a little muriate of ammonia is mixed with the paste; and when the ball has become dry, it is cautiously ignited at the flame of a spirit lamp. The sal ammoniac, escaping from

all parts of the mass, gives it a degree of porosity which is peculiarly favourable to its action. The ball, thus prepared, should be protected from dust, and be heated to redness just before being used. To insure accuracy, the hydrogen employed should be kept over mercury for a few hours in contact with a platinum ball and a piece of caustic potassa. The first deprives it of traces of oxygen which it commonly contains, and the second of moisture and sulphuretted hydrogen. The analysis must be performed in a mercurial trough. The time required for completely removing the oxygen depends on the diameter of the tube. If the mixture is contained in a very narrow tube, the diminution does not arrive at its full extent in less than twenty minutes or half an hour; while in a vessel of an inch in diameter, the effect is complete in the course of five minutes.

*Mode of determining the Quantity of Nitrogen in Gaseous Mixtures.*—As atmospheric air, which has been deprived of moisture and carbonic acid, consists of oxygen and nitrogen only, the proportion of the latter is of course known as soon as that of the former is determined. The only method, indeed, by which chemists are enabled to estimate the quantity of this gas, is by withdrawing the other gaseous substances with which it is mixed.

*Mode of determining the Quantity of Carbonic Acid in Gaseous Mixtures.*—When carbonic acid is the only acid gas which is present, as happens in atmospheric air, in the ultimate analysis of organic compounds, and in most other analogous researches, the process for determining its quantity is exceedingly simple; for it consists merely in absorbing that gas by lime-water, or a solution of caustic potassa. This is easily done in the course of a few minutes in an ordinary graduated tube; or it may be effected almost instantaneously by agitating the gaseous mixture with the alkaline solution in Hope's eudiometer. This apparatus, as represented in the figure, is formed of two parts; the bottle A, capable of containing about twenty drachms of fluid, and furnished with a well-ground stopper C; and of the tube B, of the capacity of one cubic inch, divided into 100 equal parts, and accurately fitted by grinding to the neck of the bottle. The tube, full of gas, is fixed into the bottle, previously filled with lime-water, and its contents are briskly agitated. The stopper C is then withdrawn under water, when a portion of liquid rushes into the tube, supplying the place of the gas which has disappeared; and the process is afterwards repeated, as long as any absorption ensues.




The eudiometer of Dr Hope was originally designed for analyzing air or other similar mixtures, the bottle being filled with a solution of the hydrosulphuret of potassa or lime, or some liquid capable of absorbing oxygen. To the employment of this apparatus it has been objected, that the absorption is rendered slow by the partial vacuum which is continually taking place within it, an inconvenience particularly felt towards the close of the process, in consequence of the eudiometric liquor being diluted by the admission of water. To remedy this defect, Dr Henry has substituted a bottle of elastic gum for that of glass, as in the annexed wood-cut, by which contrivance no vacuum can occur. From the improved method of analyzing air, however, this instrument is now rarely employed in eudiometry; but it may be used with advantage

for absorbing carbonic acid or similar gases, and is particularly useful for the purpose of demonstration.

*Mode of analyzing Mixtures of Hydrogen and other Inflammable Gases.*—When hydrogen is mixed with nitrogen, air, or other similar gaseous mixtures, its quantity is easily ascertained by causing it to combine with oxygen, either by means of platinum, or the electric spark. If, instead of hydrogen, any other combustible substance, such as carbonic oxide, light carburetted hydrogen, or olefiant gas, is mixed with nitrogen, the analysis is easily effected by adding a sufficient quantity of oxygen, and detonating the mixture by electricity. The diminution in volume indicates the quantity of hydrogen contained in the gas, and from the carbonic acid, which may then be removed by an alkali, the quantity of carbon is inferred*.

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* It is not easy to perceive how the diminution in volume will indicate the quantity of hydrogen contained in the gas. If Dr Turner means that in cases of the mixture of *free* hydrogen, either with nitrogen or air, that explosion with an excess of oxygen will indicate the quantity of hydrogen present, by the diminution in volume, it being two-thirds of that diminution, the fact is readily admitted; but with regard to the other supposed mixtures, the rule given is obviously inexact. Not to speak of the case of carbonic oxide, which is evidently inapplicable, as that gas contains no hydrogen, it will be found on examination, that where either light carburetted hydrogen, or olefiant gas is mixed with nitrogen, no conclusion can be drawn from the diminution of volume; and for this reason, that in these combustible gases, the hydrogen exists already condensed; and besides it is impossible to know beforehand how much of the oxygen may be expended in the formation of carbonic acid.

In the case of a mixture of nitrogen and light carburetted hydrogen, the experimenter being certain that no other gas is present, it would be easy to ascertain the quantity of the latter. All that would be necessary to be done, would be to explode the mixture with an excess of oxygen, measure the carbonic acid formed, deduce the carbon present in it, and calculate how much hydrogen the carbon would require to convert it into light carburetted hydrogen. By proceeding in a similar manner, a mixture of nitrogen and olefiant gas might be analyzed.

Where the mixture consists of nitrogen and carbonic oxide, the volume of the carbonic acid formed will indicate the volume of this oxide.

If a mixture is supposed of nitrogen, carbonic oxide, light carburetted hydrogen, olefiant gas, and free hydrogen, the analysis is somewhat complicated. The first step will be the removal of the olefiant gas by the method of Dr Henry, by means of chlorine. The next is to determine the precise quantity of oxygen necessary for the complete combustion of the residue. This is ascertained by detonating the mixture with an excess of oxygen, absorbing the carbonic acid formed, and analyzing the new residue (which necessarily consists of nitrogen and the excess of oxygen) by means of hydrogen. The oxygen in excess, thus ascertained, being deducted from the whole quantity employed, will give the amount expended in the explosion. The quantity of carbonic acid formed will give the quantity of carbon in the mixture, and this amount, together with the weight of the nitrogen, deducted from the total weight of the gas after the removal of the olefiant gas, will give the weight of the oxygen and hydrogen

An elegant mode of converting carbonic oxide into carbonic acid gas, suggested by Dr Henry, is to mix it with rather more than its own volume of nitrous oxide gas, and fire the mixture by the electric spark. The two gases mutually decompose each other, and give rise to nitrogen and carbonic acid gases. For each measure of carbonic oxide, one of carbonic acid is produced, one measure of nitrous oxide is decomposed, and one of nitrogen evolved. By employing a slight excess of pure carbonic oxide, the composition of nitrous oxide may be ascertained. The mixed gases occupy the same space after deflagration as before it; and the carbonic acid gas occupies the same space as the nitrous oxide, which had been present. (Annals of Philosophy, xxiv. 301.)

When olefiant gas is mixed with other inflammable gases, its quantity is easily determined by an elegant and simple process proposed by Dr Henry. (Page 236.) It consists in mixing 100 measures, or any convenient quantity of the gaseous mixture, with an equal volume of chlorine in a vessel covered with a piece of cloth or paper, so as to protect it from light; and after an interval of about ten minutes, the excess of chlorine is removed by lime-water or potassa. The loss experienced by the gas to be analyzed, indicates the exact quantity of olefiant gas which it had contained.

This method is not correct when the vapours of the dense hydrocarburets are present. Thus when oil gas is mixed with chlorine, the diminution in volume arises from the removal of the combustible vapours as well as of olefiant gas; for the former are equally disposed as the latter to unite with chlorine.

In mixtures of hydrogen, carburetted hydrogen, and carbonic oxide, the analytic process is exceedingly difficult and complicated, and requires all the resources of the most refined chemical knowledge, and all the address of an experienced analyst. The most recent information on this subject will be found in Dr Henry's Essay in the Philosophical Transactions for 1824.

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present. The oxygen in the carbonic acid formed, deducted from that expended in the explosion, will give the oxygen which has been expended in the formation of water; and this oxygen, added to the oxygen and hydrogen present in the gas, will give the weight of the water formed. From the weight of the water, the hydrogen present in it may be inferred, and this deducted from the aggregate weight of the oxygen and hydrogen in the gas, will give the weight of the oxygen present. This oxygen, by the supposition, must have existed in the carbonic oxide; and by calculation, the quantity of carbon it would require to be converted into that oxide may be ascertained. This carbon deducted from the total carbon in the mixture, will give that present in the light carburetted hydrogen. The carbon being ascertained in this gas, its hydrogen may be inferred. This hydrogen deducted from the total hydrogen present, will then give the free hydrogen. B.

## SECTION II.

### *ANALYSIS OF MINERALS.*

As the very extensive nature of this department of analytical chemistry renders a selection necessary, I shall confine my remarks solely to the analysis of those earthy minerals, with which the beginner usually commences his labours. The most common constituents of these compounds are silica, alumina, iron, manganese, lime, magnesia, potassa, soda, and the carbonic and sulphuric acids; and I shall, therefore, endeavour to give short directions for determining the quantity of each of these substances.

In attempting to separate two or more fixed principles from each other, the first object of the analytical chemist is to bring them into a state of solution. If they are soluble in water, this fluid is preferred to every other menstruum; but if not, an acid or any convenient solvent may be employed. In many instances, however, the substance to be analyzed resists the action even of the acids, and in that case the following method is adopted:—The compound is first crushed by means of a hammer or steel mortar, and is afterwards reduced to an impalpable powder in a mortar of agate: it is then intimately mixed with three, four, or more times its weight of potassa, soda, baryta, or their carbonates; and, lastly, the mixture is exposed in a crucible of silver or platinum to a strong heat. During the operation, the alkali combines with one or more of the constituents of the mineral; and, consequently, its elements being disunited, it no longer resists the action of the acids.

*Analysis of Marble or Carbonate of Lime.*—This analysis is easily made by exposing a known quantity of marble for about half an hour to a full white heat, by which means the carbonic acid gas is entirely expelled, so that by the loss in weight the quantity of each ingredient, supposing the marble to have been pure, is at once determined. In order to ascertain that the whole loss is owing to the escape of carbonic acid, the quantity of this gas may be determined by a comparative analysis. Into a small flask containing muriatic acid diluted with two or three parts of water, a known quantity of marble is gradually added, the flask being inclined to one side in order to prevent the fluid from being flung out of the vessel during the effervescence. The diminution in weight experienced by the flask and its contents, indicates the quantity of carbonic acid which has been expelled.

Should the carbonate suffer a greater loss in the fire than when decomposed by an acid, it will most probably be found to contain water. This may be ascertained by heating a piece of it to redness in a glass tube, the sides of which will be bedewed with moisture, if water is present. Its quantity may be determined by causing the watery vapour to pass through a weighed tube filled with fragments of the chloride of calcium, by which the moisture is absorbed.

*Separation of Lime and Magnesia.*—The more common kinds of carbonate of lime frequently contain traces of siliceous and aluminous earths, in consequence of which they are not completely dissolved in dilute muriatic acid. A very frequent source of impurity is carbonate of magnesia, which is often present in such quantity that it forms a peculiar compound called *magnesian limestone.* The analysis of this

substance, so far as respects carbonic acid, is the same as that of marble. The separation of the two earths may be conveniently effected in the following manner. The solution of the mineral in muriatic acid is evaporated to perfect dryness in a flat dish or *capsule* of porcelain, and after redissolving the residuum in a moderate quantity of distilled water, a solution of the oxalate of ammonia is added as long as a precipitate ensues. The oxalate of lime is then allowed to subside, collected on a filter, converted into quicklime by a white heat, and weighed; or the oxalate may be decomposed by a red heat, and after moistening the resulting carbonate with a strong solution of carbonate of ammonia, in order to supply any particles of quicklime with carbonic acid, it should be dried, heated to low redness, and regarded as pure carbonate of lime. To the filtered liquid, containing the magnesia, an excess of carbonate of ammonia, and then phosphate of soda is added, when the magnesia in the form of the ammoniaco-phosphate is precipitated. Of this precipitate, heated to redness, 100 parts, according to Stromeyer, correspond to 37 of pure magnesia.

*Earthy Sulphates.*—The most abundant of the earthy sulphates is that of lime. The analysis of this compound is easily effected. By boiling it for fifteen or twenty minutes with a solution of twice its weight of carbonate of soda, double decomposition ensues; and the carbonate of lime, after being collected on a filter and washed with hot water, is either heated to low redness to expel the water, and weighed, or at once reduced to quicklime by a white heat. Of the dry carbonate, fifty parts correspond to twenty-eight of lime. The alkaline solution is acidulated with muriatic acid, and the sulphuric acid thrown down by muriate of baryta. From the sulphate of this earth, collected and dried at a red heat, the quantity of acid may easily be estimated.

The method of analyzing the sulphates of strontia and baryta is somewhat different. As these salts are difficult of decomposition in the moist way, the following process is adopted. The sulphate, in fine powder, is mixed with three times its weight of carbonate of soda, and the mixture heated to redness in a platinum crucible for the space of an hour. The ignited mass is then digested in hot water, and the insoluble earthy carbonate collected on a filter. The other parts of the process are the same as the foregoing.

*Mode of analyzing Compounds of Silica, Alumina, and Iron.*—Minerals, thus constituted, are decomposed by an alkaline carbonate, at a red heat, in the same manner as sulphate of baryta. The mixture is afterwards digested in dilute muriatic acid, by which means all the ingredients of the mineral, if the decomposition is complete, are dissolved. The solution is next evaporated to dryness, the heat being carefully regulated towards the close of the process, in order to prevent any of the chloride of iron, the volatility of which is considerable, from being dissipated in vapour. By this operation, the silica, though previously held in solution by the acid, is entirely deprived of its solubility; so that on digesting the dry mass in water acidulated with muriatic acid, the alumina and iron are taken up, and the silica is left in a state of purity. The siliceous earth, after subsiding, is collected on a filter, carefully edulcorated, heated to redness, and weighed.

To the clear liquid, containing peroxide of iron and alumina, a solution of pure potassa is added in moderate excess; so as not only to throw down those oxides, but to dissolve the alumina. The peroxide of iron is then collected on a filter, edulcorated carefully until the washings cease to have an alkaline reaction, and is well dried on a sand bath. Of this hydrated peroxide, forty-nine parts contain forty

of anhydrous peroxide of iron. But the most accurate mode of determining its quantity is by expelling the water by a red heat. This operation, however, should be done with care; since any adhering particles of paper, or other combustible matter, would bring the iron into the state of black oxide, a change which is known to have occurred by the iron being attracted by a magnet.

To procure the alumina, the liquid in which it is dissolved is boiled with sal ammoniac, when the muriatic acid unites with the potassa, the volatile alkali is dissipated in vapour, and the alumina subsides. As soon as the solution is thus rendered neutral, the hydrous alumina is collected on a filter, dried by exposure to a white heat, and quickly weighed after removal from the fire.

*Separation of Iron and Manganese.*—A compound of these metals or their oxides may be dissolved in muriatic acid. If the iron is in a large proportion compared with the manganese, the following process may be adopted with advantage. To the cold solution, considerably diluted with water, and acidulated with muriatic acid, carbonate of soda is gradually added, and the liquid is briskly stirred with a glass rod during the effervescence, in order that it may become highly charged with carbonic acid. By neutralizing the solution in this manner, it at length attains a point at which the peroxide of iron is entirely deposited, leaving the liquid colourless; while the manganese, by aid of the free carbonic acid, is kept in solution. The iron, after subsiding, is collected on a filter, and its quantity determined in the usual manner. The filtered liquid is then boiled with an excess of the carbonate of soda; and the precipitated carbonate of manganese is collected, heated to full redness in an open crucible, by which it is converted into the red oxide, and weighed. This method is one of some delicacy; but in skilful hands it affords a very accurate result. It may also be employed for separating iron from magnesia and lime as well as from manganese.

But if the proportion of iron is small compared with that of manganese, the best mode of separating it is by succinate of ammonia or soda, prepared by neutralizing a solution of succinic acid with either of those alkalies. That this process should succeed, it is necessary that the iron be wholly in a state of peroxide, that the solution be exactly neutral, which may easily be insured by the cautious use of ammonia, and that the reddish-brown coloured succinate of iron be washed with cold water. Of this succinate, well dried at a temperature of 212° F, 90 parts correspond to 40 of the peroxide. From the filtered liquid, the manganese may be precipitated at a boiling temperature by carbonate of soda, and its quantity determined in the way above mentioned. The benzoate may be substituted for the succinate of ammonia in the preceding process.

It may be stated as a general rule, that whenever it is intended to precipitate iron by means of the alkalies, the succinates, or benzoates, it is essential that this metal be in the maximum of oxidation. It is easily brought into this state by digestion with a little nitric acid.

*Separation of Manganese from Lime and Magnesia.*—If the quantity of the former be proportionally small, it is precipitated as a sulphuret by the hydrosulphuret of ammonia or potassa. This sulphuret is then dissolved in muriatic acid, and the manganese thrown down as usual by means of an alkali. But if the manganese be the chief ingredient, the best method is to precipitate it at once, together with the two earths, by a fixed alkaline carbonate at a boiling temperature. The precipitate, after being exposed to a low red heat and weighed, is put into cold water acidulated with a drop or two of nitric

acid, when the lime and magnesia will be slowly dissolved with effervescence. Should a trace of the manganese be likewise taken up, it may easily be thrown down by the hydrosulphuret of ammonia.

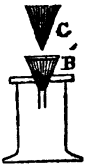
*Mode of analyzing an Earthy Mineral, containing Silica, Iron, Alumina, Manganese, Lime, and Magnesia.*—The mineral, reduced to fine powder, is ignited with three or four times its weight of carbonate of potassa or soda, the mass is taken up in dilute muriatic acid, and the silica separated in the way already described. To the solution, thus freed from silica, and duly acidulated, carbonate of soda, or still better the bicarbonate, is gradually added, so as to charge the liquid with carbonic acid, as in the analysis of iron and manganese. In this manner the iron and alumina are alone precipitated, substances, which may be separated from each other by means of pure potassa. (Page 544.) The manganese, lime, and magnesia, may be determined by the processes already described.

*Analysis of Minerals containing a Fixed Alkali.*—When the object is to determine the quantity of fixed alkali, such as potassa or soda, it is of course necessary to abstain from the employment of these reagents in the analysis itself; and the beginner will do well to devote his attention to the alkaline ingredients only. On this supposition, he will proceed in the following manner. The mineral is reduced to a very fine powder, mixed intimately with six times its weight of the artificial carbonate of baryta, and exposed for an hour to a white heat. The ignited mass is dissolved in dilute muriatic acid, and the solution evaporated to perfect dryness. The soluble parts are taken up in hot water; an excess of the carbonate of ammonia is added; and the insoluble matters, consisting of silica, carbonate of baryta, and all the constituents of the mineral, excepting the fixed alkali, are collected on a filter. The clear solution is evaporated to dryness in a porcelain capsule, and the dry mass is heated to redness in a crucible of platinum, in order to expel the salts of ammonia. The residue is the chloride of potassium or sodium.

In this analysis, it generally happens that traces of manganese, and sometimes of iron, escape precipitation in the first part of the process; and, in that case, they should be thrown down by hydrosulphuret of ammonia. If neither lime nor magnesia is present, the alumina, iron, and manganese, may be separated by pure ammonia, and the baryta subsequently removed by the carbonate of that alkali. By this method the carbonate of baryta is recovered in a pure state, and may be reserved for another analysis. The baryta may also be thrown down as a sulphate by sulphuric acid, in which case, the soda or potassa is procured in combination with that acid.

The analysis is attended with considerable inconvenience, when magnesia happens to be present; because this earth is not completely precipitated either by ammonia or its carbonate; and, therefore, some of it remains with the fixed alkali. The best mode with which I am acquainted for effecting its separation, is the following. The carbonate of ammonia is first added, and the phosphoric acid is dropped into the liquid, until all the magnesia is thrown down in the form of ammoniaco-magnesian phosphate. The excess of phosphoric acid is afterwards removed by acetate of lead, and that of lead by sulphuretted hydrogen. The acetate of the alkali is then brought to dryness, ignited, and by the addition of sulphate of ammonia converted into a sulphate.

In the preceding account, several operations have been alluded to, which, from their importance, deserve more particular mention.




The process of filtering, for example, is one on which the success of analyses materially depends. Filtration is effected by means of a glass funnel B, into which a filter C, of nearly the same size and form, made of white bibulous paper, is inserted. For researches of delicacy, the filter, before being used, is macerated for a day or two in water acidulated with nitric acid, in order to dissolve lime and other substances contained in common paper, and it is afterwards washed with hot water till every trace of acid is removed. It is next dried at 212°, or any fixed temperature insufficient to decompose it, and then carefully weighed, the weight being marked upon it with a pencil. As dry paper absorbs hygrometric moisture rapidly from the atmosphere, the filter, while being weighed, should be inclosed in a light box made for the purpose. When a precipitate is collected on a filter, it is washed with pure water until every trace of the original liquid is removed. It is subsequently dried and weighed, as before, and the weight of the paper subtracted from the combined weight of the filter and precipitate. The trouble of weighing the filter may sometimes be dispensed with. Some substances, such as silica, alumina, and lime, which are not decomposed when heated with combustible matter, may be put into a crucible while yet contained in the filter, the paper being set on fire before it is placed in the furnace. In these instances, the ash from the paper, the average weight of which is determined by previous experiments, must be subtracted from the weight of the heated mass.

The tests commonly employed in ascertaining the acidity or alkalinity of liquids are litmus and turmeric paper. The former is made by digesting litmus, reduced to a fine powder, in a small quantity of water, and painting with it white paper which is free from alum. The turmeric paper is made in a similar manner; but the most convenient test of alkalinity is litmus paper reddened by a dilute acid.

## SECTION III.

### *ANALYSIS OF MINERAL WATERS.*

Rain water collected in clean vessels in the country, or freshly fallen snow when melted, affords the purest kind of water which can be procured without having recourse to distillation. The water obtained from these sources, however, is not absolutely pure, but contains a portion of carbonic acid and air, absorbed from the atmosphere. It is remarkable that this air is very rich in oxygen. That procured from snow-water by boiling, was found by Gay-Lussac and Humboldt to contain 34.8, and that from rain water 32 per cent of oxygen gas. From the powerfully solvent properties of water, this fluid no sooner reaches the ground and percolates through the soil, than it dissolves some of the substances which it meets with in its passage. Under common circumstances, it takes up so small a quantity of foreign matter that its sensible properties are not materially affected, and in this state it gives rise to *spring*, *well*, and *river* water. Sometimes, on the contrary, it becomes so strongly impregnated with saline and other substances, that it acquires a peculiar flavour, and is

thus rendered unfit for domestic uses. It is then known by the name of *mineral water*.

The composition of spring water is dependent on the nature of the soil through which it flows. If it has filtered through primitive strata, such as quartz rock, granite, and the like, it is in general very pure; but if it meets with limestone or gypsum in its passage, a portion of these salts is dissolved, and communicates the property called *hardness*. Hard water is characterized by decomposing soap, the lime of the former yielding an insoluble compound with the acid* of the latter. If this defect is owing to the presence of carbonate of lime, it is easily remedied by boiling, when free carbonic acid is expelled, and the insoluble carbonate of lime subsides. If sulphate of lime is present, the addition of a little carbonate of soda, by precipitating the lime, converts the hard into soft water. Besides these ingredients, the muriates of lime and soda are frequently contained in spring water.

Spring water, in consequence of its saline impregnation, is frequently unfit for chemical purposes, and on these occasions distilled water is employed. Distillation may be performed on a small scale by means of a retort, in the body of which water is made to boil, while the condensed vapour is received in a glass flask, called a *recipient*, which is adapted to its beak or open extremity. This process is more conveniently conducted, however, by means of a still.

The different kinds of mineral water may be conveniently arranged for the purpose of description in the six divisions of acidulous, alkaline, chalybeate, sulphurous, saline, and siliceous springs.

1. Acidulous springs, of which those of Seltzer, Spa, Pyrmont, and Carlsbad are the most celebrated, commonly owe their acidity to the presence of free carbonic acid, in consequence of the escape of which they sparkle when poured from one vessel into another. Such carbonated waters communicate a red tint to litmus paper before, but not after being boiled, and the redness disappears on exposure to the air. Mixed with a sufficient quantity of lime-water, they become turbid from the deposition of carbonate of lime. They frequently contain the carbonates of lime, magnesia, and iron, in consequence of the facility with which these salts are dissolved by water charged with carbonic acid.

The best mode of determining the quantity of carbonic acid is by heating a portion of the water in a flask, as in the annexed figure, and receiving the carbonic acid, by means of a bent tube, in a graduated jar filled with mercury.

2. Alkaline waters are such as contain a free or carbonated alkali, and, consequently, either in their natural state or when concentrated by evaporation, possess an alkaline reaction.

These springs are rare. The best instance I have met with is in water collected at the Furnas, St. Michaels, South America, and sent to the Royal Society of Edinburgh by Lord Napier. These springs

* Dr Turner no doubt alludes here to the margaric and oleic acids, into which the oil used in the fabrication of soap is converted by saponification. B.

contain carbonate of soda and carbonic acid, and are almost entirely free from earthy substances. Most of five different kinds of these waters which I examined, also contained protoxide of iron, sulphuretted hydrogen, and muriate of soda.

3. The chalybeate waters are characterized by a strong, styptic, inky taste, and by striking a black colour with the infusion of gall-nuts. The iron is sometimes combined with muriatic or sulphuric acid; but most frequently it is in the form of a carbonate of the protoxide, held in solution by free carbonic acid. On exposure to the air, the protoxide is oxidized, and the hydrated peroxide subsides, causing the ochreous deposite, so commonly observed in the vicinity of chalybeate springs.

To ascertain the quantity of iron contained in a mineral water, a known weight of it is concentrated by evaporation, and the iron brought to the state of peroxide by means of nitric acid. The peroxide is then precipitated by an alkali and weighed; and if lime and magnesia are present, it may be separated from those earths by the process described in the last section.

Chalybeate waters are by no means uncommon; but the most noted in Britain are those of Tunbridge, Cheltenham, and Brighton. The Bath water also contains a small quantity of iron.

4. The sulphurous waters, of which the springs of Aix la Chapelle, Harrogate, and Moffat afford examples, contain sulphuretted hydrogen, and are easily recognised by their odour, and by causing a brown precipitate with a salt of lead or silver. The gas is readily expelled by boiling, and its quantity may be inferred by transmitting it through a solution of acetate of lead, and weighing the sulphuret which is generated.

5. Those mineral springs are called saline which do not belong to either of the preceding divisions. The salts which are most frequently contained in these waters, are the sulphates, muriates, and carbonates, of lime, magnesia, and soda. Potassa sometimes exists in them, and Berzelius has found lithia in the spring of Carlsbad. It has lately been discovered that the presence of hydriodic acid in small quantity is not unfrequent*. As examples of saline water may be enumerated the springs of Epsom, Cheltenham, Bath, Bristol, Barèges, Buxton, Pitcaithly, and Toeplitz.

The first object in examining a saline spring is to determine the nature of its ingredients. Muriatic acid is detected by nitrate of silver, and sulphuric acid by muriate of baryta; and if an alkaline carbonate be present, the precipitate occasioned by either of these tests will contain a carbonate of silver or baryta. The presence of lime and magnesia may be discovered, the former by oxalate of ammonia, and the latter by carbonate of ammonia and phosphoric acid. Potassa is known by the action of muriate of platinum. (Page 284.) To detect soda, the water should be evaporated to dryness, the deliquescent salts removed by alcohol, and the matter insoluble in that menstruum taken up by a small quantity of water, and allowed to crystallize by spontaneous evaporation. The salt of soda may then be recognised by the rich yellow colour which it communicates to flame. (Page 286.) If the presence of hydriodic acid is suspected, the solution is brought to dryness, the soluble parts dissolved in two or three drachms of a

* The salt spring at Theodorshalle, in Germany, contains a considerable quantity of bromine. See note page 218. B.

cold solution of starch, and strong sulphuric acid gradually added. (Page 214.)

Having thus ascertained the nature of the saline ingredients, their quantity may be determined by evaporating a pint of water to dryness, heating to low redness, and weighing the residue. In order to make an exact analysis, a given quantity of the mineral water is concentrated in an evaporating basin as far as can be done without causing either precipitation or crystallization, and the residual liquid is divided into two equal parts. From one portion the sulphuric and carbonic acids are thrown down by nitrate of baryta, and after collecting the precipitate on a filter, the muriatic acid is precipitated by nitrate of silver. The mixed sulphate and carbonate is exposed to a low red heat, and weighed; and the latter is then dissolved by dilute muriatic acid, and its quantity determined by weighing the sulphate. The chloride of silver, of which 146 parts correspond to 37 of muriatic acid, is fused in a platinum spoon or crucible, in order to render it quite free from moisture. To the other half of the concentrated mineral water, oxalate of ammonia is added for the purpose of precipitating the lime; and the magnesia is afterwards thrown down as the ammoniaco-phosphate, by means of the carbonate of ammonia and phosphoric acid. Having thus determined the weight of each of the fixed ingredients, excepting the soda, the loss of course gives the quantity of that alkali; or it may be procured in a separate state by the process described in the foregoing section.

The individual constituents of the water being known, it remains to determine the state in which they were originally combined. In a mineral water containing sulphuric and muriatic acids, lime and soda, it is obvious that three cases are possible. The liquid may contain sulphate of lime and muriate of soda, or muriate of lime and sulphate of soda, or each acid may be distributed between both the bases. It was at one time supposed that the lime must be in combination with sulphuric acid, because the sulphate of that earth is left when the water is evaporated to dryness. This, however, by no means follows. In whatever state the lime may exist in the original spring, gypsum will be generated as soon as the concentration reaches that degree at which sulphate of lime cannot be held in solution. The late Dr Murray*, who treated this question with much sagacity, observes that some mineral waters, which contain the four principles above mentioned, possess higher medicinal virtues than can be justly ascribed to the presence of sulphate of lime. He advances the opinion that alkaline bases are united in mineral waters with those acids with which they form the most soluble compounds, and that the insoluble salts obtained by evaporation are merely products. He therefore proposes to arrange the substances determined by analysis according to this supposition. To this practice there is no objection; but it is probable that each acid is rather distributed between several bases than combined exclusively with one of them. (Page 108.)

Sea-water may be regarded as one of the saline mineral waters. Its taste is disagreeably bitter and saline, and its fixed constituents amount to about three per cent. Its specific gravity varies from 1.0269 to 1.0285; and it freezes at about 28.5° F. According to the analysis of Dr Murray, 10,000 parts of water from the frith of Forth contain 220.01 parts of common salt, 33.16 of sulphate of soda, 42.08 of muriate of magnesia, and 7.84 of muriate of lime. Dr Wollaston has de-

* Philosophical Transactions of Edinburgh, vol. vii.

tected potassa in sea-water, and it likewise contains small quantities of hydriodic and hydrobromic acids.

The water of the Dead Sea has a far stronger saline impregnation than sea-water, containing one-fourth of its weight of solid matter. It has a peculiarly bitter, saline, and pungent taste, and its specific gravity is 1.211. According to the analysis of Dr Marcet, 100 parts of it are composed of muriate of magnesia 10.246, muriate of soda 10.36, muriate of lime 3.92, and sulphate of lime 0.054. In the river Jordan, which flows into the Dead Sea, Dr Marcet discovered the same principles as in the lake itself.

6. Siliceous waters are very rare, and in those hitherto discovered the silica appears to have been dissolved by means of soda. The most remarkable of these are the boiling springs of the Geyser and Rykum in Iceland, a gallon of which, according to the analysis of Dr Black, contains the following substances: (Edinburgh Philos. Trans. iii. 95.)

| | *Geyser.* | *Rykum.* |
|---|---|---|
| Soda, | 5.56 | 3.0 |
| Alumina, | 2.80 | 0.29 |
| Silica, | 31.50 | 21.83 |
| Muriate of soda, | 14.42 | 16.96 |
| Sulphate of soda, | 8.57 | 7.53 |

The hot springs of Pinnarkoon and Loorgootha are analogous to the foregoing. A gallon of the water yields about 24 grains of solid matter; and the saline contents sent to Dr Brewster by Mr P. Breton, I found to contain 21.5 per cent of silica, 19 chloride of sodium, 19 sulphate of soda, 19 carbonate of soda, pure soda 5, and 15.5 water. (Edinburgh Journal of Science, No. xvii. p. 97.)

## ERRATA.

Page 36, line 25, for numerator, *read* denominator. This error occurs only in part of the impression. Page 41, line 18, for 180°, *read* 680°. Page 473, line 18, for bases, *read* basis.

# APPENDIX.

## TABLE I.

*TABLE of Chemical Equivalents, Atomic Weights, or Proportional Numbers, Hydrogen being taken as unity.*

IN preparing the following tabular view of the atomic weights, I have chiefly consulted the table published by Dr Thomson in his First Principles of Chemistry, and by Mr Phillips in the new series, 10th volume, of the Annals of Philosophy. From the full account already given of the Laws of Combination and of the Atomic Theory, it will be superfluous to describe the uses of the table. The only explanation required on this subject, relates to the ingenious contrivance of Dr Wollaston, called the *Scale of Chemical Equivalents.* This useful instrument is a table of atomic weights, comprehending all those substances, which are most frequently employed by chemists in the laboratory; and it only differs from other tabular arrangements of the same kind, in the numbers being attached to a sliding rule, which is divided according to the principle of that of Gunter. From the mathematical construction of the scale, it not only serves the same purpose as other tables of atomic weights, but in many instances supersedes the necessity of calculation. Thus, by inspecting the common table of atomic weights, we learn that 88 parts, or one equivalent of sulphate of potassa, contain 40 parts of sulphuric acid and 48 of potassa; but recourse must be had to calculation, when it is wished to determine the quantity of acid or alkali in any other quantity of the salt. This knowledge, on the contrary, is obtained directly by means of the scale of chemical equivalents. For example, on pushing up the slide, until 100 marked upon it is in a line with the name sulphate of potassa on the fixed part of the scale, the numbers opposite to the terms sulphuric acid and potassa, will give the precise quantity of each contained in 100 parts of the compound. In the original scale of Dr Wollaston, for a particular account of which I may refer to the Philosophical Transactions for 1814, oxygen is taken as the standard of comparison; but hydrogen may be selected for that purpose with equal propriety, and scales of this kind have been prepared for sale by Mr Boswell Reid of Edinburgh.

| | |
|---|---|
| Acid, acetic, (51 Prout) | 50 |
| c. 1w.* | 59 |
| arsenic, (a. 38 + ox. 20 Berz.) | 58 |
| arsenious, (a. 38 + ox. 12 Berz.) | 50 |
| benzoic | 120 |
| boracic, (b. 8 + ox. 16) | 24 |
| c. 2w. | 42 |
| bromic, (b. 75 + ox. 40) | 115 |
| carbonic, (carb. 6 + ox. 16) | 22 |
| chloric, (chl. 36 + ox. 40) | 76 |
| chloriodic, (chl. 72 + iod. 124) | ?196 |
| chlorocarbonic, (chl. 36 + carb. oxide 14) | 50 |
| chlorocyanic, (chl. 36 + cyan. 26) | 62 |
| chromic, (chr. 32 + ox. 20) | 52 |
| citric, | 58 |
| c. 2w. | 76 |
| columbic, | ?209 |
| fluoboric, | ?68 |
| formic, | 37 |
| fluosilicic, | ?26.86 |
| gallic, | ?63 |
| hydriodic, (iod. 124 + hyd. 1) | 125 |
| hydrobromic, (b. 75 + hyd. 1) | 76 |
| hydrocyanic, (cyan. 26 + hyd. 1) | 27 |
| hydrofluoric, | 19.86 |
| hyposulphurous, (s. 32 + ox. 8) | 40 |
| hyposulphuric, (s. 32 + ox. 40) | 72 |
| iodic, (iod. 124 + ox. 40) | 164 |
| malic, | ?70 |
| manganeseous, | ?52 |
| manganesic, | ?60 |
| molybdic, | 72 |
| muriatic, (chl. 36 + hyd. 1) | 37 |
| Acid, nitric, dry, (nit. 14 + ox. 40) | 54 |
| nitric, liquid (sp. gr. 1.5) (2w.) | 72 |
| nitrous (nit. 14 + ox. 32) | 46 |
| oxalic, | 36 |
| c. 4w. (3w. Prout) | 72 |
| perchloric, (chl. 36 + ox. 56) | 92 |
| phosphorous, (p. 15.71 + ox. 12) | 27.71 |
| phosphoric, (p. 15.71 + ox. 20) | 35.71 |
| saccholactic, | ?104 |
| selenious, (sel. 40 + ox. 16) | 56 |
| selenic, (sel. 40 + ox. 24) | 64 |
| succinic, | 50 |
| sulphuric, dry, (s. 16 + ox. 24) | 40 |
| sulphuric, liquid, (sp. gr. 1.8485,) (1w.) | 49 |
| sulphurous, (s. 16 + ox. 16) | 32 |
| tartaric, | 66 |
| c. 1w. | 75 |
| titanic, | 48 |
| tungstic, | 120 |
| uric, (90 Prout) | 72 |
| Alcohol, (ol. gas 14 + aq. vap. 9) | 23 |
| Alum, anhydrous, | 262 |
| c. 25w. | 487 |
| Alumina, | 18 |
| sulphate, | 58 |
| Aluminium, | 10 |
| Ammonia, (nit. 14 + hyd. 3) | 17 |
| Antimony, | 44 |
| chloride, (ant. 44 + chl. 36) | 80 |
| iodide, (ant. 44 + iod. 124) | 168 |
| protoxide, (ant. 44 + ox. 8) | 52 |
| deutoxide, (ant. 44 + ox. 12) | 56 |

* C means crystallized, w, water; and the numeral before w expresses the number of equivalents of water which the crystals contain.

| | |
|---|---|
| Antimony, peroxide, (ant. 44 + ox. 16) | 60 |
| sulphuret, . . | 60 |
| Arsenic, . . | 38 |
| sulphuret, (realgar) | 54 |
| sesquisulphuret* (orpiment) . . | 62 |
| persulphuret, (a. 38 + s. 40) . | 78 |
| Barium, . . | 70 |
| chloride, . . | 106 |
| iodide, . . | 194 |
| protoxide, (baryta) | 78 |
| peroxide, . . | 86 |
| phosphuret, . | 85.71 |
| sulphuret, . . | 86 |
| Bismuth, . . | 72 |
| chloride, . . | 108 |
| oxide, . . | 80 |
| iodide, . . | 196 |
| phosphuret, | 87.71 |
| sulphuret, . | 88 |
| Boron, . . | 8 |
| Bromine, . . | ?75 |
| Cadmium, . . | 56 |
| chloride, . . | 92 |
| oxide, . . | 64 |
| iodide, . . | 180 |
| phosphuret, . | 71.71 |
| sulphuret, . . | 72 |
| Calcium, . . | 20 |
| chloride, . . | 56 |
| iodide, . . | 144 |
| protoxide, (lime) . | 28 |
| phosphuret, . | 35.71 |
| sulphuret, . . | 36 |
| Carbon, . . | 6 |
| bisulphuret, (carb. 6. + s. 32) . | 38 |
| chloride, . . | 42 |
| perchloride, (carb. 12 + chl. 108) . | 120 |
| oxide, . . | 14 |
| phosphuret, . | 21.71 |
| Cerium, . . | 50 |
| protoxide, (cer. 50 + ox. 8) . . | 58 |
| peroxide, (cer. 50 + ox. 12) . | 62 |
| Chlorine, . . | 36 |

| | |
|---|---|
| Chlorine, hydrocarburet, (chl. 36. + ol. gas 14) | 50 |
| protoxide, (chl. 36 + ox. 8) . . | 44 |
| peroxide, (chl. 36 + ox. 32) . . | 68 |
| Chromium, . . | 32 |
| protoxide, . . | 40 |
| Cobalt, (29.5 Rothoff) | 26 |
| chloride, . . | 62 |
| iodide, . . | 150 |
| protoxide, (cob. 26 + ox. 8) . | 34 |
| peroxide, (cob. 26 + ox. 12) . | 38 |
| phosphuret, . | 41.71 |
| sulphuret, . . | 42 |
| Columbium, . . | ?185 |
| Copper, (32 Thomson) | 64 |
| chloride, . . | 100 |
| bichloride, . . | 136 |
| iodide, . . | 188 |
| protoxide, . . | 72 |
| peroxide, . . | 80 |
| phosphuret, . | 79.71 |
| sulphuret, . . | 80 |
| bisulphuret, . | 96 |
| Cyanogen, (carb. 12 + nit. 14.) . . | 26 |
| bisulphuret, (cyan. 26 + s. 32) . | 58 |
| Ether, (ol. gas 28 + aq. vap. 9) . . | 37 |
| Fluorine, . . | 18.86 |
| Glucinium, . . | 18 |
| Glucina, . . | 26 |
| Gold, . . . | 200 |
| chloride, . . | 236 |
| bichloride, . . | 272 |
| iodide, . . | 324 |
| protoxide, (g. 200 + ox. 8) . . | ?208 |
| peroxide, (g. 200 + ox. 24) . . | ?224 |
| sulphuret, (g. 200 + s. 48) . . | 248 |
| Hydrogen, . . | 1 |
| arseniuretted, . | 39 |
| carburetted, (carb. 6 + hyd. 2) . . | 8 |

* 1 proportional of arsenic, and 1½ sulphur.

| | |
|---|---|
| **Hydrogen**, bicarb. (ol. gas) (carb. 12 + hyd. 2) | 14 |
| seleniuretted, | 41 |
| sulphuretted, | 17 |
| bisulphuretted, | 33 |
| **Iodine**, | 124 |
| **Iridium**, | ? 30 |
| **Iron**, | 28 |
| chloride, (ir. 28 + chl. 36) | 64 |
| perchloride, (ir. 28 + chl. 54) | 82 |
| iodide, | 152 |
| protoxide, (ir. 28 + ox. 8) | 36 |
| peroxide, (ir. 28 + ox. 12) | 40 |
| sulphuret, | 44 |
| bisulphuret, | 60 |
| **Lead**, | 104 |
| chloride, | 140 |
| protoxide, (l. 104 + ox. 8) | 112 |
| deutoxide, (l. 104 + ox. 12) | 116 |
| peroxide, (l. 104 + ox. 16) | 120 |
| phosphuret, | 119.71 |
| sulphuret, | 120 |
| **Lithium**, | 10 |
| chloride, | 46 |
| iodide, | 134 |
| oxide, (lithia) | 18 |
| sulphuret, | 26 |
| **Magnesium**, | 12 |
| chloride, | 48 |
| oxide, (magnesia) | 20 |
| sulphuret, | 28 |
| **Manganese**, | 28 |
| chloride, (m. 28 + chl. 36) | 64 |
| perchloride, (m. 28 + chl. 144) | 172 |
| protoxide, (m. 28 + ox. 8) | 36 |
| deutoxide, (m. 28 + ox. 12) | 40 |
| peroxide, (m. 28 + ox. 16) | 44 |
| sulphuret, | 44 |
| **Mercury**, | 200 |
| chloride, (calomel) | 236 |
| bichloride, (corros. sub.) | 272 |
| **Mercury**, iodide, | 324 |
| biniodide, | 448 |
| protoxide, | 208 |
| peroxide, | 216 |
| sulphuret, | 216 |
| bisulphuret, | 232 |
| **Molybdenum**, | 48 |
| protoxide, (m. 48 + ox. 8) | 56 |
| deutoxide, (m. 48 + ox. 16) | 64 |
| peroxide (molybdic acid) (m. 48 + ox. 24) | 72 |
| **Nickel**, | 26 |
| chloride, | 62 |
| iodide, | 150 |
| protoxide, (n. 26 + ox. 8) | 34 |
| peroxide, (n. 26 + ox. 12) | 38 |
| phosphuret, | 41.71 |
| sulphuret, | 42 |
| **Nitrogen**, | 14 |
| bicarburet, (cyanogen) | 26 |
| chloride, (n. 14 + chl. 144) | 158 |
| iodide, (n. 14 + iod. 372) | 386 |
| protoxide, (n. 14 + ox. 8) | 22 |
| deutoxide, (n. 14 + ox. 16) | 30 |
| **Oxygen**, | 8 |
| **Palladium**, | 56 |
| oxide, | 64 |
| **Phosphorus**, | 15.71 |
| chloride, | 51.71 |
| bichloride, | 87.71 |
| carburet, | 21.71 |
| sulphuret, | 31.71 |
| **Platinum**, | 96 |
| chloride, | 132 |
| bichloride, | 168 |
| protoxide, | 104 |
| deutoxide, | 112 |
| sulphuret, | 112 |
| bisulphuret, | 128 |
| **Potassium**, | 40 |
| chloride, | 76 |
| iodide, | 164 |
| protoxide, (potassa) | 48 |
| peroxide, (p. 40 + ox. 24) | 64 |

| | |
|---|---|
| Potassium, phosphuret, | 55.71 |
| sulphuret, . . | 56 |
| Rhodium, . . | 44 |
| protoxide, . . | 52 |
| peroxide, . . | 60 |
| Selenium, . . | 40 |
| Silica, . . . | 16 |
| Silicium, . . | 8 |
| Silver, . . | 110 |
| chloride, . . | 146 |
| iodide, . . | 234 |
| oxide, . . | 118 |
| phosphuret, . | 125.71 |
| sulphuret, . . | 126 |
| Sodium, . . | 24 |
| chloride, . . | 60 |
| iodide, . . | 148 |
| protoxide, (soda) . | 32 |
| peroxide, (s. 24 + ox. 12) . . | 36 |
| phosphuret, . | 39.71 |
| sulphuret, . . | 40 |
| Strontium, . . | 44 |
| chloride, . . | 80 |
| iodide, . . | 168 |
| protoxide, (strontia) | 52 |
| phosphuret, . | 59.71 |
| sulphuret, . . | 60 |
| Sulphur, . . | 16 |
| chloride, . . | 52 |
| iodide, . . | 140 |
| phosphuret, . | 31.71 |
| Sulphuretted hydrogen, | 17 |
| Tellurium, (Berzelius) | 32 |
| chloride, . . | 68 |
| oxide, . . | 40 |
| Tin, . . . . | 58 |
| chloride, . . | 94 |
| bichloride, . . | 130 |
| protoxide, . . | 66 |
| deutoxide, . . | 74 |
| phosphuret, . | 73.71 |
| sulphuret, . . | 74 |
| bisulphuret, . | 90 |
| Titanium, . . | 32 |
| protoxide, . . | ?40 |
| deutoxide (titanic acid) | 48 |
| Tungsten, . . | 96 |
| deutoxide, (brown) (t. 96 + ox. 16) . | 112 |
| tritoxide (tungstic acid) (t. 96 + ox. 24) . | 120 |



| | |
|---|---|
| Uranium, . . | 208 |
| protoxide, . . | 216 |
| deutoxide, . . | 224 |
| Water, . . | 9 |
| Yttrium, . . | 34 |
| oxide, (yttria) . | 42 |
| Zinc, . . . | 34 |
| chloride, . . | 70 |
| oxide, . | 42 |
| phosphuret, . | 49.71 |
| sulphuret, . . | 50 |
| Zirconium, . . | ?25 |
| Zirconia, . . | ?33 |

## *Salts.*

| | |
|---|---|
| Acetate of alumina, . | 68 |
| c. 1w. . . | 77 |
| ammonia, . . . | 67 |
| c. 7w. . . . | 130 |
| baryta, . . | 128 |
| c. 3w. . . | 155 |
| cadmium, (c. 2w.) . | 132 |
| copper, (acid 50 + perox. 80) . | 130 |
| c. 6w. (com. verdigris) . . | 184 |
| binacetate, . | 180 |
| c. 3w. (distilled verdigris) . | 207 |
| subacetate, . | 210 |
| lead, . . | 162 |
| c. 3w. . . | 189 |
| lime, . . | 78 |
| magnesia, . . | 70 |
| mercury, (c. 4w.) . | 294 |
| potassa, . . | 98 |
| silver, . . | 168 |
| strontia, (c. 1w.) . | 111 |
| zinc, . . | 92 |
| c. 7w. . . | 155 |
| Arseniate of lead, . | 170 |
| lime, . . | 86 |
| magnesia, . . | 78 |
| potassa, . . | 106 |
| binarseniate, (c. 2w.) | 182 |
| soda, . . | 90 |
| binarseniate, (c. 4w.) | 184 |
| strontia, . . | 110 |
| silver, . . | 176 |
| Arsenite of lime, . | 78 |
| potassa, . . | 98 |
| soda, . . | 82 |

| | |
|---|---|
| Arsenite of silver, | 168 |
| Carbonate of | |
| ammonia, | 39 |
| sesquicarb. (acid 33 + am. 17 + w. 9) | 59 |
| bicarbonate (1w.) | 70 |
| baryta, | 100 |
| copper, (acid 22 + perox. 80) | 102 |
| iron, (acid 22 + protox. 36) | 58 |
| lead, | 134 |
| lime, | 50 |
| magnesia, | 42 |
| manganese, | 58 |
| potassa, | 70 |
| bicarbonate, | 92 |
| c. 1w. | 101 |
| soda, | 54 |
| c. 10w. | 144 |
| bicarbonate, (c. 1w.) | 85 |
| strontia, | 74 |
| zinc, | 64 |
| Chlorate of baryta, | 154 |
| lead, | 188 |
| mercury, | 284 |
| potassa, | 124 |
| Chromate of baryta, | 130 |
| lead, | 164 |
| mercury, | 260 |
| potassa, | 100 |
| bichromate, | 152 |
| Muriate of ammonia, | 54 |
| baryta, (c. 1w.) | 124 |
| lime, (c. 6w.) | 119 |
| magnesia, | 57 |
| strontia, (c. 8w.) | 161 |
| Nitrate of ammonia, | 71 |
| baryta, | 132 |
| bismuth, (c. 3w.) | 161 |
| lead, | 166 |
| lime, | 82 |
| magnesia, | 74 |
| mercury, (acid 54 + protox. 208 + w. 18) | 280 |
| potassa, | 102 |
| silver, | 172 |
| soda, | 86 |
| strontia, | 106 |
| Oxalate of ammonia, | 53 |
| c. 2w. | 71 |
| baryta, | 114 |
| binoxalate, | 150 |
| cobalt, | 70 |
| Oxalate of lime, | 64 |
| nickel, | 70 |
| potassa, | 84 |
| c. 1w. | 93 |
| binoxalate, | 120 |
| c. 2w. | 138 |
| quadroxalate, | 192 |
| c. 7w. | 255 |
| strontia, | 88 |
| binoxalate, | 124 |
| Phosphate of ammonia, (c. 2w.) | 70.71 |
| baryta, | 113.71 |
| lead, | 147.71 |
| lime, | 63.71 |
| magnesia, | 55.71 |
| soda, | 67.71 |
| c. 12½w. | 180.21 |
| Sulphate of alumina, | 58 |
| alumina and potassa, | 262 |
| c. 25w. (alum) | 487 |
| ammonia, (c. 1w.) | 66 |
| baryta, | 118 |
| copper, (acid 40 + perox. 80) | 120 |
| bipersulphate, | 160 |
| c. 10w. (blue vitriol) | 250 |
| iron, | 76 |
| c. 7w. (green vitriol) | 139 |
| lead, | 152 |
| lime, | 68 |
| c. 2w. | 86 |
| lithia, (c. 1w.) | 67 |
| magnesia, (c. 7w.) | 123 |
| mercury, (acid 40 + perox. 216) | 256 |
| bipersulphate (acid 80 + perox. 216) | 296 |
| potassa, | 88 |
| bisulphate, (c. 2w.) | 146 |
| soda, | 72 |
| c. 10w. | 162 |
| strontia, | 92 |
| zinc, | 82 |
| c. 7w. | 145 |
| Tartrate of lead, | 178 |
| lime, | 94 |
| potassa, | 114 |
| bitartrate, | 180 |
| c. 2w. (cream of tartar) | 198 |
| antimony and potassa, (c. 3w.)(tartar emetic) | 363 |

## TABLE II.

***TABLE of the Elastic Force of Aqueous Vapour at Different Temperatures, expressed in Inches of Mercury.***

| Temp: | Force of Vapour. | | Temp. | Force of Vapour. | | Temp. | Force of Vapour. | |
|---|---|---|---|---|---|---|---|---|
| | Dalton | Ure | | Dalton | Ure | | Dalton | Ure |
| 32° F. | 0.200 | 0.200 | 72° F. | 0.770 | | 112° F. | 2.68 | |
| 33 | 0.207 | | 73 | 0.796 | | 113 | 2.76 | |
| 34 | 0.214 | | 74 | 0.823 | | 114 | 2.84 | |
| 35 | 0.221 | | 75 | 0.851 | 0.860 | 115 | 2.92 | 2.820 |
| 36 | 0.229 | | 76 | 0.880 | | 116 | 3.00 | |
| 37 | 0.237 | | 77 | 0.910 | | 117 | 3.08 | |
| 38 | 0.245 | | 78 | 0.940 | | 118 | 3.16 | |
| 39 | 0.254 | | 79 | 0.971 | | 119 | 3.25 | |
| 40 | 0.263 | 0.250 | 80 | 1.00 | 1.010 | 120 | 3.33 | 3.300 |
| 41 | 0.273 | | 81 | 1.04 | | 121 | 3.42 | |
| 42 | 0.283 | | 82 | 1.07 | | 122 | 3.50 | |
| 43 | 0.294 | | 83 | 1.10 | | 123 | 3.59 | |
| 44 | 0.305 | | 84 | 1.14 | | 124 | 3.69 | |
| 45 | 0.316 | | 85 | 1.17 | 1.170 | 125 | 3.79 | 3.830 |
| 46 | 0.328 | | 86 | 1.21 | | 126 | 3.89 | |
| 47 | 0.339 | | 87 | 1.24 | | 127 | 4.00 | |
| 48 | 0.351 | | 88 | 1.28 | | 128 | 4.11 | |
| 49 | 0.363 | | 89 | 1.32 | | 129 | 4.22 | |
| 50 | 0.375 | 0.360 | 90 | 1.36 | 1.360 | 130 | 4.34 | 4.366 |
| 51 | 0.388 | | 91 | 1.40 | | 131 | 4.47 | |
| 52 | 0.401 | | 92 | 1.44 | | 132 | 4.60 | |
| 53 | 0.415 | | 93 | 1.48 | | 133 | 4.73 | |
| 54 | 0.429 | | 94 | 1.53 | | 134 | 4.86 | |
| 55 | 0.443 | 0.416 | 95 | 1.58 | 1.640 | 135 | 5.00 | 5.070 |
| 56 | 0.458 | | 96 | 1.63 | | 136 | 5.14 | |
| 57 | 0.474 | | 97 | 1.68 | | 137 | 5.29 | |
| 58 | 0.490 | | 98 | 1.74 | | 138 | 5.44 | |
| 59 | 0.507 | | 99 | 1.80 | | 139 | 5.59 | |
| 60 | 0.524 | 0.516 | 100 | 1.86 | 1.860 | 140 | 5.74 | 5.770 |
| 61 | 0.542 | | 101 | 1.92 | | 141 | 5.90 | |
| 62 | 0.560 | | 102 | 1.98 | | 142 | 6.05 | |
| 63 | 0.578 | | 103 | 2.04 | | 143 | 6.21 | |
| 64 | 0.597 | | 104 | 2.11 | | 144 | 6.37 | |
| 65 | 0.616 | 0.630 | 105 | 2.18 | 2.100 | 145 | 6.53 | 6.600 |
| 66 | 0.635 | | 106 | 2.25 | | 146 | 6.70 | |
| 67 | 0.655 | | 107 | 2.32 | | 147 | 6.87 | |
| 68 | 0.676 | | 108 | 2.39 | | 148 | 7.05 | |
| 69 | 0.698 | | 109 | 2.46 | | 149 | 7.23 | |
| 70 | 0.721 | 0.726 | 110 | 2.53 | 2.456 | 150 | 7.42 | 7.530 |
| 71 | 0.745 | | 111 | 2.60 | | 151 | 7.61 | |

TABLE II. CONTINUED.

| Temp. | Force of Vapour. | | Temp. | Force of Vapour. | | Temp. | Force of Vapour. | |
|---|---|---|---|---|---|---|---|---|
| | Dalton | Ure | | Dalton | Ure | | Dalton | Ure |
| 152° F. | 7.81 | | 197° F. | 22.13 | | 242° F. | 51.34 | 53.600 |
| 153 | 8.01 | | 198 | 22.69 | | 243 | 52.18 | |
| 154 | 8.20 | | 199 | 23.16 | | 244 | 53.03 | |
| 155 | 8.40 | 8.500 | 200 | 23.64 | 23.600 | 245 | 53.88 | 56.340 |
| 156 | 8.60 | | 201 | 24.12 | | 246 | 54.68 | |
| 157 | 8.81 | | 202 | 24.61 | | 247 | 55.54 | |
| 158 | 9.02 | | 203 | 25.10 | | 248 | 56.42 | 60.400 |
| 159 | 9.24 | | 204 | 25.61 | | 249 | 57.31 | |
| 160 | 9.46 | 9.600 | 205 | 26.13 | 25.900 | 250 | 58.21 | 61.900 |
| 161 | 9.68 | | 206 | 26.66 | | 251 | 59.12 | 63.500 |
| 162 | 9.91 | | 207 | 27.20 | | 252 | 60.05 | |
| 163 | 10.15 | | 208 | 27.74 | | 253 | 61.00 | |
| 164 | 10.41 | | 209 | 28.29 | | 254 | 61.92 | 66.700 |
| 165 | 10.68 | 10.800 | 210 | 28.84 | 28.880 | 255 | 62.85 | 67.25 |
| 166 | 10.96 | | 211 | 29.41 | | 256 | 63.76 | |
| 167 | 11.25 | | 212 | 30.00 | 30.000 | 257 | 64.82 | 69.800 |
| 168 | 11.54 | | 213 | 30.60 | | 258 | 65.78 | |
| 169 | 11.83 | | 214 | 31.21 | | 259 | 66.75 | |
| 170 | 12.13 | 12.050 | 215 | 31.83 | | 260 | 67.73 | 72.300 |
| 171 | 12.43 | | 216 | 32.46 | 33.400 | 261 | 68.72 | |
| 172 | 12.73 | | 217 | 33.09 | | 262 | 69.72 | 75.900 |
| 173 | 13.02 | | 218 | 33.72 | | 263 | 70.73 | |
| 174 | 13.32 | | 219 | 34.35 | | 264 | 71.74 | 77.900 |
| 175 | 13.62 | 13.550 | 220 | 34.99 | 35.540 | 265 | 72.76 | 78.040 |
| 176 | 13.92 | | 221 | 35.63 | 36.700 | 266 | 73.77 | |
| 177 | 14.22 | | 222 | 36.25 | | 267 | 74.79 | 81.900 |
| 178 | 14.52 | | 223 | 36.88 | | 268 | 75.80 | |
| 179 | 14.83 | | 224 | 37.53 | | 269 | 76.82 | 84.900 |
| 180 | 15.15 | 15.160 | 225 | 38.20 | 39.110 | 270 | 77.85 | 86.300 |
| 181 | 15.50 | | 226 | 38.89 | 40.100 | 271 | 78.89 | 88.000 |
| 182 | 15.86 | | 227 | 39.59 | | 272 | 79.94 | |
| 183 | 16.23 | | 228 | 40.30 | | 273 | 80.98 | 91.200 |
| 184 | 16.61 | | 229 | 41.02 | | 274 | 82.01 | |
| 185 | 17.00 | 16.900 | 230 | 41.75 | 43.100 | 275 | 83.13 | 93.480 |
| 186 | 17.40 | | 231 | 42.49 | | 276 | 84.35 | |
| 187 | 17.80 | | 232 | 43.24 | | 277 | 85.47 | 97.800 |
| 188 | 18.20 | | 233 | 44.00 | | 278 | 86.50 | |
| 189 | 18.60 | | 234 | 44.78 | 46.800 | 279 | 87.63 | 101.600 |
| 190 | 19.00 | 19.000 | 235 | 45.58 | 47.220 | 280 | 88.75 | 101.900 |
| 191 | 19.42 | | 236 | 46.39 | | 281 | 89.87 | 104.400 |
| 192 | 19.86 | | 237 | 47.20 | | 282 | 90.99 | |
| 193 | 20.32 | | 238 | 48.02 | 50.300 | 283 | 92.11 | 107.700 |
| 194 | 20.77 | | 239 | 48.84 | | 284 | 93.23 | |
| 195 | 21.22 | 21.100 | 240 | 49.67 | 51.700 | 285 | 94.35 | 112.200 |
| 196 | 21.68 | | 241 | 50.50 | | 286 | 95.48 | |

TABLE II. CONTINUED.

| Temp. | Force of Vapour. | | Temp. | Force of Vapour. | | Temp. | Force of Vapour. | |
|---|---|---|---|---|---|---|---|---|
| | Dalton | Ure | | Dalton | Ure | | Dalton | Ure |
| 287° F. | 96.64 | 114.800 | 300° F. | 111.81 | 139.700 | 313° F. | 127.00 | |
| 288 | 97.80 | | 301 | 112.98 | | 314 | 128.15 | |
| 289 | 98.96 | 118.200 | 302 | 114.15 | 144.300 | 315 | 129.29 | |
| 290 | 100.12 | 120.150 | 303 | 115.32 | 147.700 | 316 | 130.43 | |
| 291 | 101.28 | | 304 | 116.50 | | 317 | 131.57 | |
| 292 | 102.45 | 123.100 | 305 | 117.68 | 150.560 | 318 | 132.72 | |
| 293 | 103.63 | | 306 | 118.86 | 154.400 | 319 | 133.86 | |
| 294 | 104.80 | 126.700 | 307 | 120.03 | | 320 | 135.00 | |
| 295 | 105.97 | 129.000 | 308 | 121.20 | 157.700 | 321 | 136.14 | |
| 296 | 107.14 | | 309 | 122.37 | | 322 | 137.28 | |
| 297 | 108.31 | 133.900 | 310 | 123.53 | 161.300 | 323 | 138.42 | |
| 298 | 109.48 | 137.400 | 311 | 124.69 | 164.800 | 324 | 139.56 | |
| 299 | 110.64 | | 312 | 125.85 | 167.000 | 325 | 140.70 | |

## TABLE III.

*Dr Ure's Table, showing the Elastic Force of the Vapours of Alcohol, Ether, Oil of Turpentine, and Petroleum or Naphtha, at Different Temperatures, expressed in Inches of Mercury.*

| Ether. | | Alcohol sp. gr. 0.813 | | Alcohol sp. gr. 0.813 | | Petroleum. | |
|---|---|---|---|---|---|---|---|
| Temp. | Force of Vap. | Temp. | Force of Vap. | Temp. | Force of Vap. | Temp. | Force of Vap. |
| 34° | 6.20 | 32° | 0.40 | 196.3° | 50.10 | 316° | 30.00 |
| 44 | 8.10 | 40 | 0.56 | 200 | 53.00 | 320 | 31 70 |
| 54 | 10.30 | 45 | 0.70 | 206 | 60.10 | 325 | 34.00 |
| 64 | 13.00 | 50 | 0.86 | 210 | 65.00 | 330 | 36.40 |
| 74 | 16.10 | 55 | 1.00 | 214 | 69.30 | 335 | 38.90 |
| 84 | 20.00 | 60 | 1.23 | 216 | 72.20 | 340 | 41.60 |
| 94 | 24.70 | 65 | 1.49 | 220 | 78.50 | 345 | 44.10 |
| 104 | 30.00 | 70 | 1.76 | 225 | 87.50 | 350 | 46.86 |
| 105 | 30.00 | 75 | 2.10 | 230 | 94.10 | 355 | 50.20 |
| 110 | 32.54 | 80 | 2.45 | 232 | 97.10 | 360 | 53.30 |
| 115 | 35.90 | 85 | 2.93 | 236 | 103.60 | 365 | 56.90 |
| 120 | 39.47 | 90 | 3.40 | 238 | 106.90 | 370 | 60.70 |
| 125 | 43.24 | 95 | 3.90 | 240 | 111.24 | 372 | 61.90 |
| 130 | 47.14 | 100 | 4.50 | 244 | 118.20 | 375 | 64.00 |
| 135 | 51.90 | 105 | 5.20 | 247 | 122.10 | Oil of Turpentine. | |
| 140 | 56.90 | 110 | 6.00 | 248 | 126.10 | Temp. | Force of Vap. |
| 145 | 62.10 | 115 | 7.10 | 249.7 | 131.40 | 304° | 30.00 |
| 150 | 67.60 | 120 | 8.10 | 250 | 132.30 | 307.6 | 32.60 |
| 155 | 73.60 | 125 | 9.25 | 252 | 138.60 | 310 | 33.50 |
| 160 | 80.30 | 130 | 10.60 | 254.3 | 143.70 | 315 | 35.20 |
| 165 | 86.40 | 135 | 12.15 | 258.6 | 151.60 | 320 | 37.06 |
| 170 | 92.80 | 140 | 13.90 | 260 | 155.20 | 322 | 37.80 |
| 175 | 99.10 | 145 | 15.95 | 262 | 161.40 | 326 | 40.20 |
| 180 | 108.30 | 150 | 18.00 | 264 | 166.10 | 330 | 42.10 |
| 185 | 116.10 | 155 | 20.30 | | | 336 | 45.00 |
| 190 | 124.80 | 160 | 22.60 | | | 340 | 47.30 |
| 195 | 133.70 | 165 | 25.40 | | | 343 | 49.40 |
| 200 | 142.80 | 170 | 28·30 | | | 347 | 51.70 |
| 205 | 151.30 | 173 | 30.00 | | | 350 | 53.80 |
| 210 | 166.00 | 178.3 | 33.50 | | | 354 | 56.60 |
| | | 180 | 34.73 | | | 357 | 58.70 |
| | | 182.3 | 36.40 | | | 360 | 60.80 |
| | | 185.3 | 39.90 | | | 362 | 62.40 |
| | | 190 | 43.20 | | | | |
| | | 193.3 | 46.60 | | | | |

## TABLE IV.

*Dr Ure's Table of the Quantity of Oil of Vitriol, of sp. gr.* 1.8485, *and of Anhydrous Acid, in* 100 *parts of dilute Sulphuric Acid at Different Densities.*

| Liquid. | Sp.Gr. | Dry. | Liquid. | Sp.Gr. | Dry. | Liquid. | Sp.Gr. | Dry. |
|---|---|---|---|---|---|---|---|---|
| 100 | 1.8485 | 81.54 | 66 | 1.5503 | 53.82 | 32 | 1.2334 | 26.09 |
| 99 | 1.8475 | 80.72 | 65 | 1.5390 | 53.00 | 31 | 1.2260 | 25.28 |
| 98 | 1.8460 | 79.90 | 64 | 1.5280 | 52.18 | 30 | 1.2184 | 24.46 |
| 97 | 1.8439 | 79.09 | 63 | 1.5170 | 51.37 | 29 | 1.2108 | 23.65 |
| 96 | 1.8410 | 78.28 | 62 | 1.5066 | 50.55 | 28 | 1.2032 | 22.83 |
| 95 | 1.8376 | 77.46 | 61 | 1.4960 | 49.74 | 27 | 1.1956 | 22.01 |
| 94 | 1.8336 | 76.65 | 60 | 1.4860 | 48.92 | 26 | 1.1876 | 21.20 |
| 93 | 1.8290 | 75.83 | 59 | 1.4760 | 48.11 | 25 | 1.1792 | 20.38 |
| 92 | 1.8233 | 75.02 | 58 | 1.4660 | 47.29 | 24 | 1.1706 | 19.57 |
| 91 | 1.8179 | 74.20 | 57 | 1.4560 | 46.48 | 23 | 1.1626 | 18.75 |
| 90 | 1.8115 | 73.39 | 56 | 1.4460 | 45.66 | 22 | 1.1549 | 1794 |
| 89 | 1.8043 | 72.57 | 55 | 1.4360 | 44.85 | 21 | 1.1480 | 17.12 |
| 88 | 1.7962 | 71.75 | 54 | 1.4265 | 44.03 | 20 | 1.1410 | 16.31 |
| 87 | 1.7870 | 70.94 | 53 | 1.4170 | 43.22 | 19 | 1.1330 | 15.49 |
| 86 | 1.7774 | 70.12 | 52 | 1.4073 | 42.40 | 18 | 1 1246 | 14.68 |
| 85 | 1.7673 | 69.31 | 51 | 1.3977 | 41.58 | 17 | 1.1165 | 13.86 |
| 84 | 1.7570 | 68.49 | 50 | 1.3884 | 40.77 | 16 | 1.1090 | 13.05 |
| 83 | 1.7465 | 67.68 | 49 | 1.3788 | 39.95 | 15 | 1.1019 | 12.23 |
| 82 | 1.7360 | 66.86 | 48 | 1.3697 | 39.14 | 14 | 1.0953 | 11.41 |
| 81 | 1.7245 | 66.05 | 47 | 1.3612 | 38.32 | 13 | 1 0887 | 10.60 |
| 80 | 1.7120 | 65.23 | 46 | 1.3530 | 37.51 | 12 | 1.0809 | 9.78 |
| 79 | 1.6993 | 64.42 | 45 | 1.3440 | 36.69 | 11 | 1.0743 | 8.97 |
| 78 | 1.6870 | 63.60 | 44 | 1.3345 | 35.88 | 10 | 1.0682 | 8.15 |
| 77 | 1.6750 | 62.78 | 43 | 1.3255 | 35.06 | 9 | 1.0614 | 7.34 |
| 76 | 1.6630 | 61.97 | 42 | 1.3165 | 34.25 | 8 | 1.0544 | 6.52 |
| 75 | 1.6520 | 61.15 | 41 | 1.3080 | 33.43 | 7 | 1.0477 | 5.71 |
| 74 | 1.6415 | 60.34 | 40 | 1.2999 | 32.61 | 6 | 1.0405 | 4.89 |
| 73 | 1.6321 | 59.52 | 39 | 1.2913 | 31.80 | 5 | 1 0336 | 4.08 |
| 72 | 1.6204 | 58.71 | 38 | 1.2826 | 30.98 | 4 | 1.0268 | 3.26 |
| 71 | 1.6090 | 57.89 | 37 | 1.2740 | 30.17 | 3 | 1.0206 | 2.446 |
| 70 | 1.5975 | 57.08 | 36 | 1.2654 | 29.35 | 2 | 1.0140 | 1.63 |
| 69 | 1.5868 | 56.26 | 35 | 1.2572 | 28.54 | 1 | 1.0074 | 0.8154 |
| 68 | 1.5760 | 55.45 | 34 | 1.2490 | 27.72 | | | |
| 67 | 1.5648 | 54.63 | 33 | 1.2409 | 26.91 | | | |

## TABLE V.

***Dr Ure's Table of the Quantity of Real or Anhydrous Nitric Acid in 100 parts of Liquid Acid at Different Densities.***

| Specific Gravity. | Real acid in 100 parts of the Liq. | Specific Gravity. | Real acid in 100 parts of the Liq. | Specific Gravity. | Real acid in 100 parts of the Liq. |
|---|---|---|---|---|---|
| 1.5000 | 79.700 | 1.3783 | 52.602 | 1.1833 | 25.504 |
| 1.4980 | 78.903 | 1.3732 | 51.805 | 1.1770 | 24.707 |
| 1.4960 | 78.106 | 1.3681 | 51.068 | 1.1709 | 23.910 |
| 1.4940 | 77.309 | 1.3630 | 50.211 | 1.1648 | 23.113 |
| 1.4910 | 76.512 | 1.3579 | 49.414 | 1.1587 | 22.316 |
| 1.4880 | 75.715 | 1.3529 | 48.617 | 1.1526 | 21.519 |
| 1.4850 | 74.918 | 1.3477 | 47.820 | 1.1465 | 20.722 |
| 1.4820 | 74.121 | 1.3427 | 47.023 | 1.1403 | 19.925 |
| 1.4790 | 73.324 | 1.3376 | 46.226 | 1.1345 | 19.128 |
| 1.4760 | 72.527 | 1.3323 | 45.429 | 1.1286 | 18.331 |
| 1.4730 | 71.730 | 1.3270 | 44.632 | 1.1227 | 17.534 |
| 1.4700 | 70.933 | 1.3216 | 43.835 | 1.1168 | 16.737 |
| 1.4670 | 70.136 | 1.3163 | 43.038 | 1.1109 | 15.940 |
| 1.4640 | 69.339 | 1.3110 | 42.241 | 1.1051 | 15.143 |
| 1.4600 | 68.542 | 1.3056 | 41.444 | 1.0993 | 14.346 |
| 1.4570 | 67.745 | 1.3001 | 40.647 | 1.0935 | 13.549 |
| 1.4530 | 66.948 | 1.2947 | 39.850 | 1.0878 | 12.752 |
| 1.4500 | 66.155 | 1.2887 | 39.053 | 1.0821 | 11.955 |
| 1.4460 | 65.354 | 1.2826 | 38.256 | 1.0764 | 11.158 |
| 1.4424 | 64.557 | 1.2765 | 37.459 | 1.0708 | 10.361 |
| 1.4385 | 63.760 | 1.2705 | 36.662 | 1.0651 | 9.564 |
| 1.4346 | 62.963 | 1.2644 | 35.865 | 1.0595 | 8.767 |
| 1.4306 | 62.166 | 1.2583 | 35.068 | 1.0540 | 7.970 |
| 1.4269 | 61.369 | 1.2523 | 34.271 | 1.0485 | 7.173 |
| 1.4228 | 60.572 | 1.2462 | 33.474 | 1.0430 | 6.376 |
| 1.4189 | 59.775 | 12402 | 32.677 | 1.0375 | 5.579 |
| 1.4147 | 58.978 | 1.2341 | 31.880 | 1.0320 | 4.782 |
| 1.4107 | 58.181 | 1 2277 | 31.083 | 1.0267 | 3.985 |
| 1.4065 | 57.384 | 1.2212 | 30.286 | 1.0212 | 3.188 |
| 1.4023 | 56.587 | 1.2148 | 29.489 | 1.0159 | 2.391 |
| 1.3978 | 55.790 | 1.2084 | 28.692 | 1.0106 | 1.594 |
| 1.3945 | 54.993 | 1.2019 | 27.895 | 1.0053 | 0.797 |
| 1.3882 | 54.196 | 1.1958 | 27.098 | | |
| 1.3833 | 53.399 | 1.1895 | 26.301 | | |

## TABLE VI.

***ble of Lowitz, showing the Quantity of Absolute Alcohol in Spirits of Different Specific Gravities.***

| 0 Parts. | | Sp. Gravity. | | 100 Parts. | | Sp. Gravity. | | 100 Parts. | | Sp. Gravity. | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| lc. | Wat. | At 68° | At 60° | Alc. | Wat. | At 68° | At 60° | Alc. | Wat. | At 68° | At 60° |
| .00 | 0 | 0.791 | 0.796 | 66 | 34 | 0.877 | 0.881 | 32 | 68 | 0.952 | 0.955 |
| 99 | 1 | 0.794 | 0.798 | 65 | 35 | 0.880 | 0.883 | 31 | 69 | 0.954 | 0.957 |
| 98 | 2 | 0.797 | 0.801 | 64 | 36 | 0.882 | 0.886 | 30 | 70 | 0.956 | 0.958 |
| 97 | 3 | 0.800 | 0.804 | 63 | 37 | 0.885 | 0.889 | 29 | 71 | 0.957 | 0.960 |
| 96 | 4 | 0.803 | 0.807 | 62 | 38 | 0.887 | 0.891 | 28 | 72 | 0.959 | 0.962 |
| 95 | 5 | 0.805 | 0.809 | 61 | 39 | 0.889 | 0.893 | 27 | 73 | 0.961 | 0.963 |
| 94 | 6 | 0.808 | 0.812 | 60 | 40 | 0.892 | 0.896 | 26 | 74 | 0.963 | 0.965 |
| 93 | 7 | 0.811 | 0.815 | 59 | 41 | 0.894 | 0.898 | 25 | 75 | 0.965 | 0.967 |
| 92 | 8 | 0.813 | 0.817 | 58 | 42 | 0.896 | 0.900 | 24 | 76 | 0.966 | 0.968 |
| 91 | 9 | 0.816 | 0.820 | 57 | 43 | 0.899 | 0.902 | 23 | 77 | 0.968 | 0.970 |
| 90 | 10 | 0.818 | 0.822 | 56 | 44 | 0.901 | 0.904 | 22 | 78 | 0.970 | 0.972 |
| 89 | 11 | 0.821 | 0.825 | 55 | 45 | 0.903 | 0.906 | 21 | 79 | 0.971 | 0.973 |
| 88 | 12 | 0.823 | 0.827 | 54 | 46 | 0.905 | 0.908 | 20 | 80 | 0.973 | 0.974 |
| 87 | 13 | 0.826 | 0.830 | 53 | 47 | 0.907 | 0.910 | 19 | 81 | 0.974 | 0.975 |
| 86 | 14 | 0.828 | 0.832 | 52 | 48 | 0.909 | 0.912 | 18 | 82 | 0.976 | 0.977 |
| 85 | 15 | 0.831 | 0.835 | 51 | 49 | 0.912 | 0.915 | 17 | 83 | 0.977 | 0.978 |
| 84 | 16 | 0.834 | 0.838 | 50 | 50 | 0.914 | 0.917 | 16 | 84 | 0.978 | 0.979 |
| 83 | 17 | 0.836 | 0.840 | 49 | 51 | 0.917 | 0.920 | 15 | 85 | 0.980 | 0.981 |
| 82 | 18 | 0.839 | 0.843 | 48 | 52 | 0.919 | 0.922 | 14 | 86 | 0.981 | 0.982 |
| 81 | 19 | 0.842 | 0.846 | 47 | 53 | 0.921 | 0.924 | 13 | 87 | 0.983 | 0.984 |
| 80 | 20 | 0.844 | 0.848 | 46 | 54 | 0.923 | 0.926 | 12 | 88 | 0.985 | 0.986 |
| 79 | 21 | 0.847 | 0.851 | 45 | 55 | 0.925 | 0.928 | 11 | 89 | 0.986 | 0.987 |
| 78 | 22 | 0.849 | 0.853 | 44 | 56 | 0.927 | 0.930 | 10 | 90 | 0.987 | 0.988 |
| 77 | 23 | 0.851 | 0.855 | 43 | 57 | 0.930 | 0.933 | 9 | 91 | 0.988 | 0.989 |
| 76 | 24 | 0.853 | 0.857 | 42 | 58 | 0.932 | 0.935 | 8 | 92 | 0.989 | 0.990 |
| 75 | 25 | 0.856 | 0.860 | 41 | 59 | 0.934 | 0.937 | 7 | 93 | 0.991 | 0.991 |
| 74 | 26 | 0.859 | 0.863 | 40 | 60 | 0.936 | 0.939 | 6 | 94 | 0.992 | 0.992 |
| 73 | 27 | 0.861 | 0.865 | 39 | 61 | 0.938 | 0.941 | 5 | 95 | 0.994 | |
| 72 | 28 | 0.863 | 0.867 | 38 | 62 | 0.940 | 0.943 | 4 | 96 | 0.995 | |
| 71 | 29 | 0.866 | 0.870 | 37 | 63 | 0.942 | 0.945 | 3 | 97 | 0.997 | |
| 70 | 30 | 0.868 | 0.872 | 36 | 64 | 0.944 | 0.947 | 2 | 98 | 0.998 | |
| 69 | 31 | 0.870 | 0.874 | 35 | 65 | 0.946 | 0.949 | 1 | 99 | 0.999 | |
| 68 | 32 | 0.872 | 0.878 | 34 | 66 | 0.948 | 0.951 | 0 | 100 | 1.000 | |
| 67 | 33 | 0.875 | 0.879 | 33 | 67 | 0.950 | 0.953 | | | | |

## TABLE VII.

***Table showing the Specific Gravity of Liquids, at the Temperature of 55° Fahr. corresponding to the Degrees of Baumé's Hydrometer.***

### For Liquids lighter than Water.

| Deg. | Sp. Gr. | Deg. | Sp. Gr. | Deg. | Sp. Gr. | Deg. | Sp. Gr. | Deg. | Sp. Gr. |
|---|---|---|---|---|---|---|---|---|---|
| 10= | 1.000 | 17= | .949 | 23= | .909 | 29= | .874 | 35= | .842 |
| 11 | .990 | 18 | .942 | 24 | .903 | 30 | .867 | 36 | .837 |
| 12 | .985 | 19 | .935 | 25 | .897 | 31 | .861 | 37 | .832 |
| 13 | .977 | 20 | .928 | 26 | .892 | 32 | .856 | 38 | .827 |
| 14 | .970 | 21 | .922 | 27 | .886 | 33 | .852 | 39 | .822 |
| 15 | .963 | 22 | .915 | 28 | .880 | 34 | .847 | 40 | .817 |
| 16 | .955 | | | | | | | | |

### For Liquids heavier than Water.

| Deg. | Sp. Gr. | Deg. | Sp. Gr. | Deg. | Sp. Gr. | Deg. | Sp. Gr. | Deg. | Sp. Gr. |
|---|---|---|---|---|---|---|---|---|---|
| 0= | 1.000 | 15= | 1.114 | 30= | 1.261 | 45= | 1.455 | 60= | 1.717 |
| 3 | 1.020 | 18 | 1.140 | 33 | 1.295 | 48 | 1.500 | 63 | 1.779 |
| 6 | 1.040 | 21 | 1.170 | 36 | 1.333 | 51 | 1.547 | 66 | 1.848 |
| 9 | 1.064 | 24 | 1.200 | 39 | 1.373 | 54 | 1.594 | 69 | 1.920 |
| 12 | 1.089 | 27 | 1.230 | 42 | 1.414 | 57 | 1.659 | 72 | 2.000 |

# GENERAL INDEX.